Electrophilic Substitution in Acenaphthene and Related Compounds. III.[1] Acetylation of Some Monosubstituted Acenaphthenes

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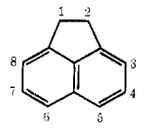
3-Acetyl-, 3-bromo-, 3-chloro-, and 3-nitroacenaphthene have been shown to acetylate exclusively in the 6 position. 3-*tert*-Butylacenaphthene also acetyles predominantly in the 6 position, in spite of preferential electronic activation of the 5 position. 5-Acetyl- and 5-acetamidoacenaphthene acetylate in position 8, while 5-*tert*-butyl- and 5-methylacenaphthene react predominantly in position 3. Reaction of 5-fluoro-, 5-chloro-, 5-bromo-, and 5-iodoacenaphthene give mixtures of the 3- and 8-acetylated products, the isomer ratio depending on the halogen (5-fluoroacenaphthene also gives 5-acetyl-6-fluoroacenaphthene). For these last compounds, partial rate factors have been obtained for substitution in the 3 and 8 positions. The halo substituents have a much smaller rate decreasing effect relative to hydrogen than in the same reaction in halobenzenes.

In part II[1] we reported on the bromination and chlorination of 3-bromo-, 3-chloro-, 5-bromo-, and 5-chloroacenaphthene as part of a detailed study of disubstitution in acenaphthene. It had previously been shown[2] that the positions para to the bridge in acenaphthene



are extremely activated to electrophilic attack. Recent detritiation studies[3] have shown that the 3(8) positions are also activated, though less so than the 5 and 6 positions. In part II it was shown that the 3-haloacenaphthenes, as expected, underwent exclusive halogenation in the 6 position. For a 5-halo substituent and attacking nucleophile with small steric requirements, the electronically activated 6 position was preferentially attacked. In the bromination of 5-bromoacenaphthene with molecular bromine, however, ir evidence indicated that approximately equal amounts of the 3,5 and 3,6 isomers were formed. This unexpected amount of the 3,5 isomer prompted us to look at acetylation of these compounds. With one exception, the bulky acetylating entity did not substitute peri to a 5 substituent, and it was possible to measure the relative amounts of 3 and 8 substitution. Many of these compounds were hitherto unknown and most have been isolated and identified. We have also included acetylation of some 3-substituted acenaphthenes. Competition experiments have also been carried out to provide information on the relative reactivities of some of the 5-substituted compounds.

As with halogenation, little was previously known about the orientation of products in acetylation of monosubstituted acenaphthenes, and the reported yields leave a significant amount of product unaccounted for. Apart from acetylation of 3-acetyl- and 5-acetylacenaphthene[4] (which gave 65 and 15%, respectively, of the 3,6 isomer), the only reported study[5] of this reaction is with 5-bromo- and 5-chloroacenaphthenes. From reaction of the former with acetyl chloride–aluminum chloride in nitrobenzene, 3-acetyl-6-bromoacenaphthene (50%) and 3-acetyl-5-bromoacenaphthene (25%) were obtained by separation of the oximes. No yields were reported from the 5-chloro compound.

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Results and Discussion

The acetylations were carried out with acetic anhydride and aluminum (or zinc) chloride in dichloroethane. Product isomer proportions in a reaction mixture were determined by nmr analysis of the acetyl region of the spectrum, or by glpc, and the results are listed in Table I. Analysis of the reaction mixture from acetylation of 5-bromoacenaphthene at various times showed that the isomer ratio was not time dependent.

TABLE I
ACETYLATION OF MONOSUBSTITUTED ACENAPHTHENES[a,b]

Substituent	% overall product yield (glpc)	Disubstituted product isomer distribution, % 3,6	3,5	5,6	3,8
3-Acetyl	>95	90			
3-Bromo	~50[c]	90			
3-*tert*-Butyl	>90	60			30
3-Chloro	~65[c]	95			
3-Nitro	~50[c]	90			
5-Acetyl	~100	92			
5-Bromo	>95	56	44		
5-Chloro	>95	63	37		
5-Fluoro	>95	30	30	40	
5-Iodo	>90	35	65		
5-Methyl	~100		>90		
5-*tert*-Butyl	~80[c]	30	70		
5-Acetamido	>95	100			

[a] Using acetic anhydride under the conditions described in the text. [b] Acetylation of acenaphthene gave 80% 5-acetyl- and 20% 3-acetylacenaphthene. [c] Remainder was largely starting material.

3-Substituted Acenaphthenes.—Table I indicates that, with one exception, acetylation occurred exclusively in the 6 position. The acetyl, bromo, chloro, and nitro substituents are all electron withdrawing, and it is therefore not surprising on electronic grounds that further substitution occurs in the other ring. These results are in accord with our previous halogenation findings.[1]

Acetylation of 3-*tert*-butylacenaphthene, however, indicates that simple electronic considerations do not

adequately explain the results. For this activating substituent, the predominant reaction should have occurred in the 5 position but the 3,6 isomer in fact predominated. In addition, more reaction occurred in the 8 position than in the 5 position. The 3-acetyl-8-*tert*-butylacenaphthene was identified from nmr and ir spectra. The aromatic proton region of the nmr spectrum contained an AB pattern (2 H, J = 9 Hz) and a singlet (2 H), inconsistent with the spectrum expected for 5-acetyl-3-*tert*-butylacenaphthene. The ir spectrum contained no strong peak around 770 cm^{-1}, characteristic of three adjacent hydrogens in acenaphthene compounds.

It seems clear that steric as well as electronic factors determine the product orientation in these reactions. Thus, for a 3-substituted acenaphthene, formation of the transition state for substitution in the 6 or 8 positions apparently allows greater relief of steric strain than does substitution in the 5 position.

5-Substituted Acenaphthenes.—Further substitution in 5-substituted acenaphthenes is complex, the position of substitution and proportions of products being quite dependent on the identity of the 5 substituent. Of special interest is the ratio of 3 (to give the 3,5 isomer) to 8 (3,6 isomer) substitution. The substitution pattern in each case was assigned from known[1] ir and nmr data.

In simplest terms, substitution in the 3 and 8 positions of a 5-substituted acenaphthene compared with acenaphthene should be electronically analogous to substitution in the meta position of a monosubstituted benzene relative to substitution in benzene. 5-Methyl- and 5-*tert*-butylacenaphthene were found to acetylate predominantly in the 3 position as expected for these donor substituents.

In contrast to the alkyl-substituted compounds, 5-acetamido- and 5-acetylacenaphthene underwent acetylation in the 8 position. More severe conditions were needed for complete reaction of these compounds, no doubt owing to some complexing of the acetylating entity with the substituent in each case, which results in considerable relative deactivation of the 3 position. Nitration of 5-acetamidoacenaphthene has been shown[6] to occur at the 4 position. The absence of this isomer in the acetylation reaction illustrates the greater effective bulk of the acetylating species. Results from acetylation of the 5-haloacenaphthenes are especially intriguing. Only with 5-fluoro was an appreciable amount of the 5,6 isomer produced. The small size of the fluoro atom evidently allows acetylation at the electronically activated peri position. On electronic grounds, the strongly electron-withdrawing halo groups were expected to operate like the acetyl and direct the electrophile to the 8 position. It is clear from the amount of 3,5 product produced, which increases from fluoro to iodo, that other factors are operating in these reactions. The competition experiments outlined below indicate their complexity.

An interesting side feature was an improved synthesis of 3-acetylacenaphthene, obtained by dehalogenation of the crude reaction product from acetylation of 5-bromoacenaphthene.

Competition Reactions.—Semiquantitative competition experiments were carried out by reacting suitable pairs of compounds with a deficiency of acetylating mixture under the standard conditions. From the total product yields (glpc) and the known product isomer distribution (Table I) for each compound, relative rates for substitution in the 3 and 8 positions were obtained. The data are given in Table II. While

TABLE II

RELATIVE ACETYLATION RATES OF SOME 5-SUBSTITUTED ACENAPHTHENES IN THE 3 AND 8 POSITIONS, FROM COMPETITION EXPERIMENT PRODUCT RATIOS

Competition compounds[a] A	B	Product response factor, A/B	Corrected total product ratio, A/B	k_3^A/k_3	k_8^A/k_8^B
Acenaphthene (1)	5-Cl	1.0	6.5	1.7[b]	1.1
5-F (2)	5-Cl	1.2	1.6	1.2	0.8
5-Cl (3)	5-Br	1.0	2.0	1.8	2.1
5-Br (4)	5-I (5)	0.8	1.5	1.1	2.4
Acenaphthene	5-Me	0.9	1.1	0.1	
5-Me (6)	5-*t*-Bu (7)	0.75	1.1	1.4	

[a] Registry numbers follow: 1, 83-32-9; 2, 6861-63-8; 3, 5209-33-6; 4, 2051-98-1; 5, 6861-64-9; 6, 17057-80-6; 7, 35210-35-6. [b] $6.5 \times 0.2 \times 0.5^c/1 \times 0.37$. [c] Statistical factor.

k_{rel} ≒ product ratio, the results indicate the order of magnitude of the relative reactivities and the order of substituent effects. Thus, for reaction at the 3 position the order Me > *t*-Bu > H > F > Cl > Br ~ I ($k_{H/I} \sim 2.5$) is obtained, and for the 8 position, H ~ Cl > F > Br > I ($k_{H/I} \sim 5$).

A number of points arise from these results.

(1) The difference between the rate of reaction of acenaphthene and of the slowest reacting halo-substituted compound is small for either position. Thus, quite marked differences in isomer distribution are produced by relatively small energy differences.

(2) The halogen order for reactivity in the 3 position (except iodo) is that commonly found for electrophilic substitution in the meta position of halobenzenes. However, the halogens have a very much reduced rate-retarding effect relative to hydrogen as compared to analogous benzenes.[7]

(3) The order Me > *t*-Bu is opposite to that found for meta reactivity in electrophilic substitution in toluene and *tert*-butylbenzene. The partial rate factors with respect to acenaphthene are of the same order of magnitude as found for alkylbenzenes.

(4) For reaction in the 8 position, the partial rate factors relative to that position in acenaphthene are F, 0.7; Cl, 1.0; Br, 0.4; I, 0.2.

With respect to the restricted range of partial rate factors observed for the halo substituents, similar results have been found in electrophilic substitution in highly activated benzenes. For example, the partial rate factors for nitration meta to the halo group in para haloanisoles compared with anisole itself have recently been shown[8] to be 0.096, 0.077, and 0.119 for chlorine, bromine, and iodine, respectively, compared with values of 0.00084, 0.0010, and 0.0112 for meta substitution of the analogous halobenzenes under the same conditions.

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Since the inductive and resonance effects for halo substituents are opposed, differences between halogen electronic effects will be small and a reactivity order based on these effects could thus be readily modified by other contributing effects.

Clearly, in 5-substituted acenaphthenes, nonbonded interactions occur between the substituent and peri hydrogen. It is likely that, as for 3-*tert*-butylacenaphthene, variation in this interaction energy during formation of the transition state could be largely responsible for the observed reactivity orders. For example, the reactivity of 5-iodoacenaphthene seems anomalous since iodobenzene usually undergoes electrophilic substitution faster in the meta position than does bromo-, chloro-, or even fluorobenzene.[7] This, together with the lower reactivity of, and greater proportion of 8 substitution from, 5-*tert*-butylacenaphthene relative to 5-methylacenaphthene suggests that steric factors are of major importance with these large substituents.

In conclusion, this work provides an extensive account of the directing effect of substituents in electrophilic substitution in monosubstituted acenaphthenes. Previous results on bromination of 5-bromoacenaphthene fit in with the pattern observed in the acetylation reaction. The reason for the observed reactivity orders is not fully apparent to us and is a further instance of the intriguing chemistry of the acenaphthene molecule.

Experimental Section

Glpc analyses were carried out on a GE-SE-30 silicone rubber column at 220–240°. Infrared spectra were run as KCl disks and $CDCl_3$ was employed as the solvent for nmr measurements, with TMS as internal standard. Microanalyses were carried out by the Australian Microanalytical Service.

Materials.—3-Bromo-, 3-chloro-, 5-bromo-, and 5-chloroacenaphthene were prepared as described in part II.[1] 5-Acetylacenaphthene,[9] mp 69° (lit. mp 69–70°), 5-fluoroacenaphthene,[10] mp 93–94° (lit. mp 94–95°), 5-iodoacenaphthene,[11] mp 62–63° (lit. mp 63–63.5°), 5-acetamidoacenaphthene,[12] mp 189–190° (lit. mp 190°), 3-*tert*-butylacenaphthene,[13] mp 63–64° (lit. mp 65–66°),, and 5-methylacenaphthene,[14] mp 93.5–94.5° (lit. mp 95–96°) were prepared by literature methods. The preparation[13] of 5-*tert*-butylacenaphthene was modified in that sublimation of the crude red oily product at *ca.* 0.3 mm (100°) gave, first, acenaphthene, and then 5-*tert*-butylacenaphthene contaminated with a little acenaphthene. Three recrystallizations from ethanol gave the product, mp 98–100° (lit.[13] mp 101.5–102°).

3-Acetylacenaphthene.—The crude mixture of 3-acetyl-5-bromo- and 3-acetyl-6-bromoacenaphthene obtained from acetylation of 10 g of 5-bromoacenaphthene ("standard" conditions; see below) was refluxed for 1.5 hr with cupric oxide (8.0 g), acetic anhydride (6.0 ml), and pyridine (40 ml). The reaction mixture was poured into 5% acetic acid (400 ml) and the product was filtered off. Soxhlet extraction (3 hr) with petroleum ether (bp 60–80°) gave, after evaporation, 3-acetylacenaphthene (5.2 g) containing some 3-acetylacenaphthylene impurity. Hydrogenation at atmospheric pressure in methanol (10% Pd/C catalyst) gave 3-acetylacenaphthene (4.8 g), mp 103.5–104.5° (lit.[15] mp 105°), after recrystallization from methanol–water.

"Standard" Conditions. A. Acetylating Mixture.—Acetic anhydride (0.5 mol) was added dropwise to a stirred mixture (10°) of anhydrous aluminum chloride (1.0 mol) in dry dichloroethane (2.5 mol). Anhydrous zinc chloride replaced the aluminum chloride for reactions of 3-*tert*-butyl-, 5-*tert*-butyl-, and 5-iodoacenaphthene.

B. Acetylation.—The acetylating mixture was added dropwise during 1 hr to a stirred solution of the compound (0.4 mol) in dry dichloroethane (3.5 mol), the temperature being maintained at *ca.* 0° throughout. The mixture was stirred for 1–24 hr (*ca.* 0°), the reaction was quenched by addition of an ice–concentrated hydrochloric acid mixture, and the organic layer was separated.

Analysis.—For acetylation of 5-methyl- and 3-substituted acenaphthenes except 3-*tert*-butylacenaphthene, glpc analysis indicated the presence of only one product, subsequently isolated in high yield. One product only was isolated, in high yield, from the acetylation of 5-acetamidoacenaphthene.

The product ratios from acetylation of 5-acetyl, 3-*tert*-butyl-, 5-*tert*-butyl-, and 5-iodoacenaphthene were obtained by glpc. For 5-bromo-, 5-chloro-, and 5-fluoroacenaphthene, product analysis was carried out by nmr, from knowledge of chemical shifts of the various product acetyl protons (Table III). Analysis of the reaction mixture from 5-fluoroacenaphthene requires more comment. The acetyl region of the reaction product nmr spectrum contained four peaks, two broad and equivalent and two sharp and equivalent. Conversion to the oximes followed by preparative tlc on silica gel with $CHCl_3$ eluent gave two bands (R_f 0.6 and R_f 0.25). The ketone with the R_f 0.25 oxime was shown by comparison with other spectra to be 5-acetyl-6-fluoroacenaphthene. The acetyl region in the nmr contained the two broad equivalent peaks, the splitting (J = 3.2 Hz) being due to the adjacent fluorine. The nmr spectrum of the ketone from the R_f 0.6 oxime contained two sharp and still equal acetyl signals. However, the ir spectrum contained peaks characteristic of both 3,6 [839 (s), 817 (s) cm^{-1}] and 3,5 [778 (s) cm^{-1}] substitution. Thus 3-acetyl-6-fluoroacenaphthene and 3-acetyl-5-fluoroacenaphthene were formed in equal amounts and were not separated. All three isomers had the same glpc retention time.

TABLE III

ACETYL PROTON CHEMICAL SHIFTS (FROM TMS) OF SOME HALOACETYLACENAPHTHENES (INFINITE DILUTION IN $CDCl_3$)

Substituents	Position						
Acetyl	3	3	3	3	3	3	5
Halogen	5-Br	6-Br	5-Cl	6-Cl	5-F	6-F	6-F
δ (ppm)	2.59	2.63	2.61	2.63	2.60	2.63	2.59[a]

[a] J = 3.2 Hz.

Where analysis of the reaction mixture showed the presence of only one major product, the solvent was removed and the residue was recrystallized from ethanol and (except 3-acetyl-6-nitroacenaphthene) vacuum sublimed at *ca.* 120–140°. The following compounds were isolated in this way.

3,6-Diacetylacenaphthene (from 3-acetyl- and 5-acetylacenaphthene) had mp 147–148° (lit.[4] mp 148–149°); ir 1122 (m), 1080 (m), 1018 (m), 988 (m), 963 (s), 837 (s), 814 (s) cm^{-1}. 6-Acetyl-3-bromoacenaphthene (from 3-bromoacenaphthene) had mp 98–100°; ir 1119 (m), 1073 (s), 961 (s), 854 (m), 833 (s), 814 (s) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}BrO$: C, 61.1; H, 4.0. Found: C, 61.0; H, 3.9. The oxime had mp 175–176°. *Anal.* Calcd for $C_{14}H_{12}BrNO$: C, 58.0; H, 4.2; Br, 27.6; N, 4.8. Found: C, 57.8; H, 4.1; Br, 27.9; N, 4.7. 6-Acetyl-3-chloroacenaphthene (from 3-chloroacenaphthene) had mp 108–109°; ir 1130 (s), 1078 (s), 960 (s), 884 (m), 861 (m), 833 (s), 815 (s) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}ClO$: C, 72.9; H, 4.8; Cl, 15.4. Found: C, 73.2; H, 5.05; Cl, 15.1. The oxime had mp 178–179°. *Anal.* Calcd for $C_{14}H_{12}ClNO$: C, 68.4; H, 4.9; Cl, 14.4; N, 5.7. Found: C, 68.3; H, 5.1; Cl, 14.5; N, 5.5. 6-Acetyl-3-nitroacenaphthene (from 3-nitroacenaphthene) had mp 217.5–218.5° (not sublimed); ir 970 (m), 956 (m), 935 (m), 845 (m), 839 (s), 800 (s), 755 (m) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}NO_3$: C, 69.7; H, 4.6; N, 5.8. Found: C, 69.7; H, 4.7; N, 5.55. The 2,4-dinitrophenylhydrazone had mp 259–260°. *Anal.* Calcd for $C_{26}H_{15}N_5O_6$: C, 57.0; H, 3.6; N, 16.6. Found: C, 56.9; H, 3.9; N, 16.5. 3-Acetyl-5-methyl-

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acenaphthene (from 5-methylacenaphthene) had mp 78–79°; ir 1141 (m), 979 (s), 866 (m), 830 (m), 770 (s), 746 (m) cm^{-1}. *Anal.* Calcd for $C_{13}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.3; H, 6.7. The oxime had mp 152–153°. *Anal.* Calcd for $C_{15}H_{15}NO$: C, 80.0; H, 6.7; N, 6.2. Found: C, 80.2; H, 6.9; N, 5.9. 6-Acetamido-3-acetylacenaphthene (from 5-acetamidoacenaphthene) had mp 218–220°; ir 1123 (m), 1110 (m), 1086 (m), 847 (s), 827 (w), 802 (s) cm^{-1}. *Anal.* Calcd for $C_{16}H_{13}NO_2$: C, 75.9; H, 6.0; N, 5.5. Found: C, 75.85; H, 6.0; N, 5.85.

In acetylations where two products were formed, the pure isomers were isolated by one of the following methods: by recrystallization of (a) the reaction mixture, (b) the oxime mixture prepared from the mother liquor of a, (c) the oxime mixture prepared from the original reaction mixture, or by preparative tlc of (d) the oxime mixture b, or (e) the oxime mixture c. Oximes were reconverted to the respective ketones by heating with 1:1 concentrated hydrochloric acid–water. The ketones were recrystallized from ethanol–water and vacuum sublimed at *ca.* 120–140°.

The following compounds were isolated in these ways.

From 5-chloroacenaphthene.—3-Acetyl-5-chloroacenaphthene (a, EtOH): mp 118–120°; ir 1170 (m), 1101 (m), 989 (m), 881 (m), 849 (m), 832 (m), 770 (s), 742 (m) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}ClO$: C, 72.9; H, 4.8; Cl, 15.4. Found: C, 72.7; H, 5.0; Cl, 15.5. Oxime, mp 138–139° (lit.[5] 140–141°). 3-Acetyl-6-chloroacenaphthene (b): mp 98.0–98.5°; ir 1080 (m), 978 (m), 863 (w), 841 (s), 822 (w), 810 (s), 724 (m) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}ClO$: C, 72.9; H, 4.8; Cl, 15.4. Found: C, 72.6; H, 4.8; Cl, 15.6. Oxime, mp 182–183° (EtOH–H_2O) (lit.[5] mp 183–184°).

From 5-bromoacenaphthene.—3-Acetyl-5-bromoacenaphthene (a, EtOH): mp 151–152° (lit.[5] mp 152–153°); ir 1096 (m), 980 (m), 876 (s), 836 (m), 827 (s), 766 (vs), 736 (s) cm^{-1}. 3-Acetyl-6-bromoacenaphthene (b): mp 89–90° (lit.[5] mp 91–92°); ir 1111 (m), 1068 (s), 1020 (w), 1009 (m), 966 (m), 954 (w), 840 (s), 816 (w), 808 (s), 710 (m) cm^{-1}. Oxime, mp 183–184° (EtOH–H_2O) (lit.[5] mp 184–185°).

From 5-fluoroacenaphthene (e, May and Baker silica gel, chloroform eluent).—5-Acetyl-6-fluoroacenaphthene: mp 114°; ir 1144 (m), 1099 (m), 1020 (m), 900 (w), 831 (s), 808 (w) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}FO$: C, 78.5; H, 5.2; F, 8.9. Found: C, 78.2; H, 5.1; F, 9.0. Oxime, mp 192–193°. *Anal.* Calcd for $C_{14}H_{12}FNO$: C, 73.35; H, 5.3; F, 8.3; N, 6.1. Found: C, 73.0; H, 5.3; F, 8.6; N, 5.9. An inseparable 1:1 mixture of 3-acetyl-5-fluoroacenaphthene and 3-acetyl-6-fluoroacenaphthene, mp 67–69°, was also obtained (see Analysis). *Anal.* Calcd for $C_{14}H_{12}FNO$: C, 78.5; H, 5.2; F, 8.9. Found: C, 78.2; H, 5.3; F, 8.9. Oxime, mp 134–135°.

From 5-iodoacenaphthene.—3-Acetyl-5-iodoacenaphthene (a, EtOH): mp 165–166°; ir 1178 (m), 970 (m), 963 (m), 834 (m), 781 (s) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}IO$: C, 52.2; H, 3.4; I, 39.4. Found: C, 52.3; H, 3.4; I, 39.3. 3-Acetyl-6-iodoacenaphthene (d, Merck Alumina G, CCl_4 eluent): mp 148°; ir 1110 (m), 990 (s), 840 (s), 805 (s) cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}IO$: C, 52.2; H, 3.4; I, 39.4. Found: C, 52.4; H, 3.6; I, 39.2. Oxime, mp 174–175°.

From 5-*tert*-Butylacenaphthene.—3-Acetyl-5-*tert*-butylacenaphthene (a, EtOH): mp 177–178°; ir 1110 (m), 969 (m), 916 (m), 885 (w), 849 (m), 795 (s), 770 (m) cm^{-1}. *Anal.* Calcd for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.6; H, 8.0. Column chromatography (alumina, 1:1 petroleum ether (bp 60–80°), CCl_4 eluent) of the residue from (a) gave a sample of the minor isomer, contaminated with 3-acetyl-5-*tert*-butylacenaphthene. *Anal.* Calcd for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.3; H, 8.1. From peaks at 833 (s), 818 (m), and 808 (s) in the ir spectrum, this isomer was identified as 3-acetyl-6-*tert*-butylacenaphthene.

From 3-*tert*-butylacenaphthene.—3-Acetyl-8-*tert*-butylacenaphthene (a, EtOH): mp 136–137°; ir 1018 (w), 955 (w), 850 (vs) cm^{-1}. *Anal.* Calcd for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.4; H, 8.0. Column chromatography [alumina, petroleum ether (bp 60–80°) eluent] of the residue from (a) gave 6-acetyl-3-*tert*-butylacenaphthene: mp 57–58° (EtOH); ir 1079 (m), 959 (m), 840 (m), 820 (s) cm^{-1}. *Anal.* Calcd for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.7; H, 8.1. A third, and minor, isomer was not separated.

Registry No.—3,6-Diacetylacenaphthene, 19732-51-5; 6-acetyl-3-bromoacenaphthene, 35210-37-8, 35210-38-9 (oxime); 6-acetyl-3-chloroacenaphthene, 35210-39-0, 35210-40-3 (oxime); 6-acetyl-3-nitroacenaphthene, 35223-25-7, 35223-26-8 (2,4-DNP); 3-acetyl-5-methylacenaphthene, 35223-27-9, 35223-28-0 (oxime); 6-acetamido-3-acetylacenaphthene, 35223-29-1; 3-acetyl-5-chloroacenaphthene, 35223-30-4; 3-acetyl-6-chloroacenaphthene, 35223-31-5; 3-acetyl-5-bromoacenaphthene, 35223-32-6; 3-acetyl-6-bromoacenaphthene, 35223-33-7; 5-acetyl-6-fluoroacenaphthene, 35223-34-8, 35261-94-0 (oxime); 3-acetyl-5-fluoroacenaphthene, 35223-35-9, 35223-36-0 (oxime); 3-acetyl-6-fluoroacenaphthene, 35223-37-1, 35223-38-2 (oxime); 3-acetyl-5-iodoacenaphthene, 35261-95-1; 3-acetyl-6-iodoacenaphthene, 35223-39-3, 35223-40-6 (oxime); 3-acetyl-5-*tert*-butylacenaphthene, 35223-41-7; 3-acetyl-6-*tert*-butylacenaphthene, 35223-42-8; 3-acetyl-8-*tert*-butylacenaphthene, 35223-43-9; 6-acetyl-3-*tert*-butylacenaphthene, 35223-44-0.

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