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SOME DERIVATIVES OF ACENAPHTHENE

F. VERNON and R. D. WILSON
Stockport College, Wellington Road South, Stockport

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Abstract—3,5,6,8-Tetranitroacenaphthene has been made. Bromination of 5-nitroacenaphthene gave 3-bromo-6-nitroacenaphthene. The previously prepared 1,5,6,7,8,8a-hexabromo-6,7,8,8a-tetrahydroacenaphthene has been further examined.

IN PRELIMINARY work relating to an investigation of halogenophenols some derivatives of acenaphthene have been prepared. On electronic grounds[1] the formula I is assigned to a tetranitro-compound. Modifications have been introduced in a preparation of 4-nitroacenaphthene.[2]

The mononitration of 5-bromoacenaphthene yielded an isomer of the product of bromination of 5-nitroacenaphthene. The nitro-derivative from 5-bromoacenaphthene has previously been reduced to 5-acenaphthenamine[3] and therefore was 5-bromo-6-nitroacenaphthene (II). By contrast, direct bromination of acenaphthene[4] has recently been cogently shown to give the 3,5-dibromo-derivative (III).[5] That 3,6-dibromoacenaphthene has not been detected as a product of bromination is surprising, but it is to be noted that the recognized 3,5-isomer has not been obtained in high yield.[4,6] Naphthalene, on being directly dibrominated, gives only the 1,4- and 1,5-isomers.[7] The steric effect of a nitro-substituent sometimes appears to be similar to that of a bromo-substituent.[8] However, where it is necessitated by overcrowding, the effective bulk of a nitro-group may be reduced by its rotation,[9] whereas that of a bromine atom cannot be altered in this way. The nitro-substituent in the compound (II) would then be expected to be not coplanar with the aromatic nucleus. Whilst the infrared absorption spectrum of the dibromoacenaphthene[4] (III) has a band at 860 cm^{-1}, that of 5-bromo-6-nitroacenaphthene (II) lacks the characteristic band, between 850 and 890 cm^{-1}, of an isolated aromatic C—H group.[10,11] The bromination of 5-nitroacenaphthene is thought to have given 3-bromo-6-nitroacenaphthene (IV),

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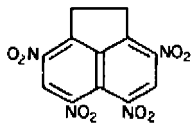

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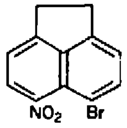

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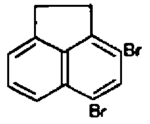

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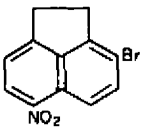

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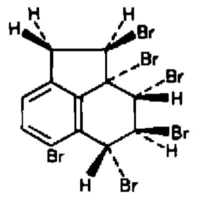
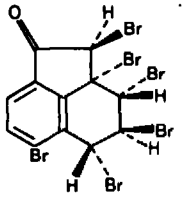


V

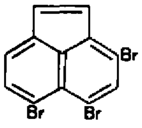


VI

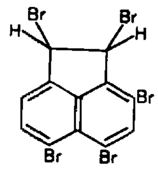
as the strong electron-withdrawal of the nitro-substituent precludes easy reaction in the 3- and 6-positions of 5-nitroacenaphthene. The spectral band at 855 cm^{-1} is attributed to the C—N vibration of the compound (IV).

The hexabromo-derivative of acenaphthene[12,13] has been further investigated. From a consideration of the steric arrangement (shown by Courtauld molecular models) and electronic effects the structure (V) and its enantiomer seem to be adequate to account for the properties of this compound. Its NMR spectrum (Fig. 2) is complex, but the AB system (τ 2·2–2·9) indicates two adjacent aromatic protons. It was oxidized to a ketone (VI and its enantiomer), the IR spectrum of which reveals a carbonyl stretching band[14] at 1725 cm^{-1}. The strong band at 1580 cm^{-1} is considered to show that the carbonyl group is conjugated with the aromatic ring. Thus the relative position of the corresponding methylene group in the precursor (V) is determined.

The compound V with potassium hydroxide has again yielded 3,5,6-tribromoacenaphthylene (VII),[12,13] which added one molar proportion of bromine to give



VII.



VIII

1,2,3,5,6-pentabromoacenaphthene (VIII). The NMR spectrum of the acenaphthylene (Fig. 3) confirms the given structure (VII). The conversion, by zinc and acetic acid, of the compound V into 5-bromoacenaphthene indicates the position of the bromo-substituent in the aromatic ring of this hexabromo-derivative. Under such reducing conditions the migration of aromatic halogen (as demonstrated by Avoyan and Struchkov[5] in the transformation of 3,5-dibromoacenaphthene into 1,8-dibromonaphthalene) seems to be impossible.

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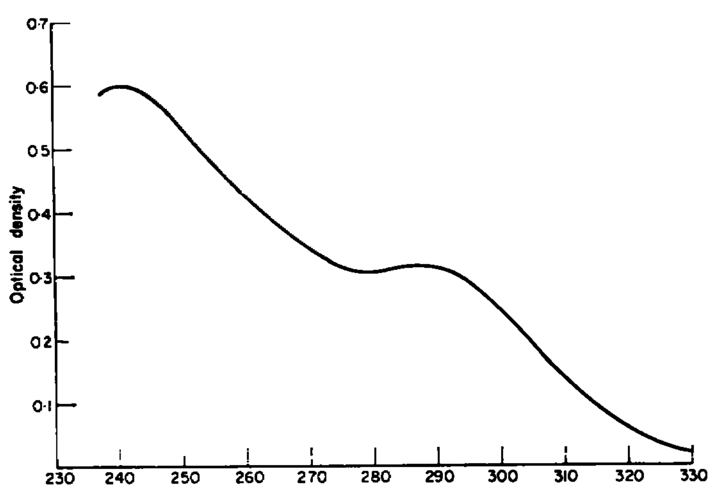

FIG. 1. Ultra-violet spectrogram of 1,5,6,7,8,8a-hexabromo-6,7,8,8a-tetrahydroacenaphthene (in cyclohexane).

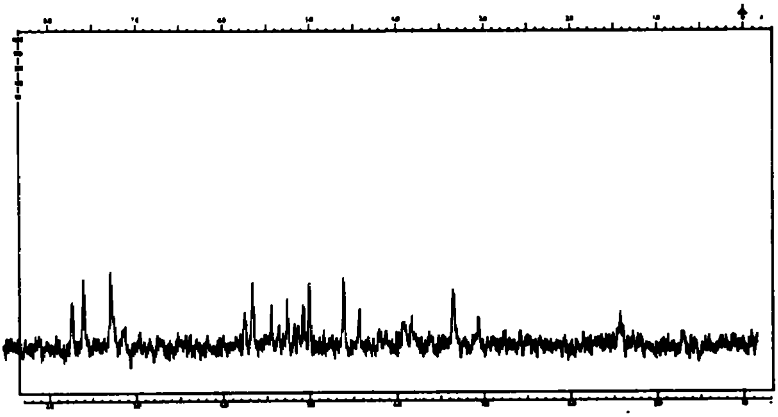

FIG. 2. NMR spectrogram of 1,5,6,7,8,8a-hexabromo-6,7,8,8a-tetrahydroacenaphthene (7% in deuteriochloroform).

EXPERIMENTAL

M.ps are uncorrected. The nuclear magnetic resonance (NMR) spectrograms were produced by a Varian A-60 instrument. The infra-red spectra were obtained from KBr discs in Perkin-Elmer 137 and 237 spectrophotometers.

3,5,6,8-*Tetranitroacenaphthene* (I). 5-Nitroacenaphthene, made from acenaphthene (20 g), was dissolved in a cold mixture of H_2SO_4 (s.g. 1·84; 500 ml) and HNO_3 (s.g. 1·51; 500 ml). After 1 week water was added. The resultant precipitate was washed (water) and recrystallized from benzene (charcoal), to give the cream-coloured *tetranitro-compound*, m.p. 212°. (Found: C, 43·0; H, 1·6. $C_{12}H_6N_4O_8$ requires: C, 43·1; H, 1·8%.)

4-*Nitroacenaphthene*. A mixture of 5-acenaphthenamine (10 g), acetic acid (10 ml) and acetic anhydride (10 ml) was refluxed for 1 hr. Dilution of the hot product with cold water (100 ml) precipitated N-5-acenaphthenylacetamide, m.p. 190° (EtOH, charcoal; lit.,[15,16,17] 238°, 184–185°,

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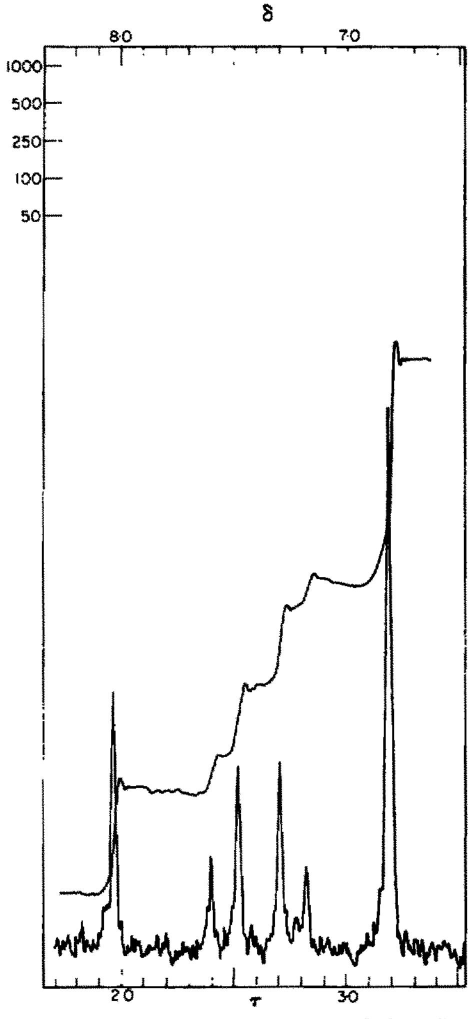

FIG. 3. NMR spectrogram of 3,5,6-tribromoacenaphthylene (in carbon tetrachloride).

192°). (Found: C, 79·7; H, 5·95; N, 7·1. Calc. for $C_{14}H_{13}NO$: C, 79·6; H, 6·2; N, 6·6%.) Whilst being cooled, this compound (7 g) in acetic acid (30 ml) was treated with HNO_3 (s.g. 1·42; 15 ml) in acetic acid (15 ml). Addition of water (200 ml) precipitated N-acetyl-4-nitro-5-acenaphthenamine (5·5 g from EtOH with charcoal; m.p. 251°; lit.[15,18,19] 255°, 242°, 251°). (Found: C, 65·4; H, 4·4; N, 11·5, 10·4. Calc. for $C_{14}H_{12}N_2O_3$: C, 65·6; H, 4·7; N, 10·9%.) To the product (at 0°) of hydrolysis[15] of the latter compound (1·12 g) by 50% v/v H_2SO_4 (50 ml) were added 0·50 M aqueous solution (9·0 ml) of $NaNO_2$ and, after 5 min, aqueous hypophosphorous acid.[20] The precipitate, dissolved in benzene, was chromatographed on alumina. Development was achieved by petroleum spirit (b.p. 60–80°)-benzene (10:1). The eluate from the lowest band afforded yellow needles of 4-nitroacenaphthene, m.p. 133° (lit.,[8] 129°). (Found: C, 72·7; H, 4·5; N, 7·0. Calc. for $C_{12}H_9NO_2$: C, 72·3; H, 4·55; N, 7·0%.)

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5-Bromo- and 3-bromo-6-nitroacenaphthene. Br$_2$ (16 g) in CHCl$_3$ was added to acenaphthene (15 g) and anhydrous FeCl$_3$ (5 g) in the same solvent. Removal (at red. press.[21]) of CHCl$_3$ from the water-washed product gave a residue, which was extracted with MeOH (8 × 50 ml). Concentration of the whole extract at 17° and diminished press. yielded 5-bromoacenaphthene (12 g), m.p. 52° (lit.,[22] 53·5–54·5°). An alternative method involved the addition of Br$_2$ in dioxan to acenaphthene in this solvent. The residue, left by removal of dioxan at 15°, was extracted with cold MeOH. Evaporation of MeOH from the extract at 15° yielded a solid, which was extracted with cold isopropanol. The material that was afforded by removal, at 15°, of the latter solvent from the extract was recrystallized from cold MeOH, to give a good yield of 5-bromoacenaphthene, m.p. 53°.

In 15 min HNO$_3$ (s.g. 1·42; 5 ml) in acetic acid (25 ml) was added to 5-bromoacenaphthene (5 g) in acetic acid (100 ml), to precipitate, in 12 hr, 5-bromo-6-nitroacenaphthene (II), m.p. 158° (benzene; lit.,[23] 160–161°). (Found: C, 51·9, 51·7; H, 2·95, 2·9; N, 5·15, 5·05. Calc. for C$_{12}$H$_8$BrNO$_2$: C, 51·8; H, 2·9; N, 5·0%), ν_{max} 461, 481, 537, 605, 640, 695, 745, 755, 800, 815 w, 830 sh, 845 s, 905, 1040, 1080, 1120 w, 1125, 1155 w, 1215, 1230, 1270 w, 1330 s, 1345 w, 1355 s, 1410, 1420, 1440, 1455 w, 1490, 1520 s, 1595, 1610, 1870 w, 2905 w cm^{-1}.[24]

To 5-nitroacenaphthene (6·7 g), dissolved in dioxan, was added, in 10 min, Br$_2$ (1·8 ml) in the same solvent. After 12 hr the product was diluted with water, to precipitate material which was crystallized successively from EtOH (charcoal), acetic acid, and benzene, to give *3-bromo-6-nitroacenaphthene* (IV), m.p. 160–161° (markedly depressed by admixture of the product of nitration of 5-bromoacenaphthene). (Found: C, 51·9; H, 2·7; N, 5·05%), ν_{max} 492, 525, 578, 705 w, 735, 755, 805 s, 820 s, 845, 855, 945, 965 w, 1010 w, 1075, 1120, 1160, 1220, 1275, 1325 s, 1350 s, 1395, 1410 w, 1440 s, 1460, 1485, 1520 s, 1585, 1610, 2925 w, 3090 w cm^{-1}.

1,5,6,7,8,8a-*Hexabromo*-6,7,8,8a-*tetrahydroacenaphthene and some derivatives.* Br$_2$ (48 g) in CHCl$_3$ was added in 4 hr to acenaphthene (15·4 g) in CHCl$_3$. After 12 hr the volatile material was removed. The residue was stirred with diethyl ether (750 ml), and the solid was filtered off and recrystallized from acetic acid, to yield the hexabromo-compound (V; 20 g), m.p. 177° (lit.,[12,23,25] dec 162–163°, m.p. 174°, m.p. 179–180°). (Found: C, 22·7, 22·8; H, 1·3, 1·4; Br, 76·0. Calc. for C$_{12}$H$_8$Br$_6$: C, 22·8; H, 1·3; Br, 75·9%), ν_{max} 685, 720 s, 730, 760 w, 785, 815 s, 835, 860 s, 920 s, 955, 960 w, 970 w, 1010, 1030, 1065 w, 1110, 1135, 1145 sh, 1160, 1190, 1210, 1240, 1270, 1295 w, 1320, 1415, 1450, 1605 w cm^{-1}. Its UV and NMR spectrograms are shown in Figs. 1 and 2.

Chromium trioxide (5 g), dissolved in water, was added to a stirred mixture of V (2 g) and acetic acid at 60°. After 12 hr the product was treated with water, to precipitate white 2,2a,3,4,5,6-*hexabromo*-2a,3,4,5-*tetrahydro*-1-*acenaphthenone* (VI), m.p. 196° (toluene; dec). (Found: C, 23·0, 22·7; H, 1·0, 1·2; Br, 72·8. C$_{12}$H$_6$Br$_6$O requires: C, 22·3; H, 0·9; Br, 74·3%), ν_{max} 497, 512, 553, 563, 581, 610, 645 s, 685, 715, 770, 785, 805 w, 840 vs, 865 w, 930, 955 w, 985 s, 1005, 1055, 1075 w, 1120, 1135, 1150 w, 1180, 1215, 1250 s, 1275 w, 1290, 1320, 1450, 1580 s, 1595, 1725 vs, 2955 w, 2975 w, 3015 w cm^{-1}. This compound was insoluble in boiling KOH aq.

A mixture of the hexabromotetrahydroacenaphthene (V), Zn and acetic acid was heated slowly to its b.p. and then refluxed for ½ hr. The filtrate from the hot product was diluted with water, to precipitate a substance which was crystallized from cold isopropanol and from cold MeOH. The resulting compound was 5-bromoacenaphthene, m.p. and mixed m.p. 53°.

A mixture of V (0·332 g) with 1:1 isopropanol–water (100 ml) and KOH (2 g) was refluxed for 30 min. The quantitatively separated filtrate from the cold product was, after acidification, equivalent to 16·4 ml of N/10 AgNO$_3$. This implied the removal of 3.1 g atoms of Br per mole the of hexabromo-compound (V). A further sample (12 g) of this compound was stirred for 12 hr in a solution of KOH (10 g) in EtOH (200 ml) and water (10 ml). Dilution with water yielded a precipitate, which was crystallized repeatedly from EtOH and from isopropanol, to furnish yellow needles of 3,5,6-tribromoacenaphthylene, m.p. 146° (lit.,[12] 143°). (Found: C, 36·6; H, 1·55. Calc. for C$_{12}$H$_5$Br$_3$: C, 37·1; H, 1·3%), ν_{max} 690 w, 720 s, 765, 805 w, 835 s, 870, 890, 910 w, 1030, 1065, 1085, 1105, 1125 s, 1205, 1320 w, 1335, 1395, 1435, 1455 w, 1490 w, 1575 w, 1605 w, 1635 w cm^{-1}. The integral curve of the

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NMR spectrogram (Fig. 3) indicates 5 protons. Specifically, these are a single (aromatic) proton, two adjacent (aromatic) protons (the AB system), and two equivalent (aliphatic) protons.

This tribromoacenaphthylene (VII), in dioxan, was treated with bromine (1 molar proportion) in the same solvent. Removal of volatile material left a residue, which was recrystallized from CCl_4, to give 1,2,3,5,6-pentabromoacenaphthene (VIII), m.p. 209° (lit.,[18] 212–213°). (Found: C, 27·0; H, 1·0. Calc. for $C_{12}H_5Br_5$: C, 26·3; H, 0·9%.)

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