Polyhalogenoaromatic Compounds. Part 52.[1] Reactions of Octachloronaphthalene with Nucleophilic Reagents and Synthesis of Some Heptachloronaphthyl Derivatives

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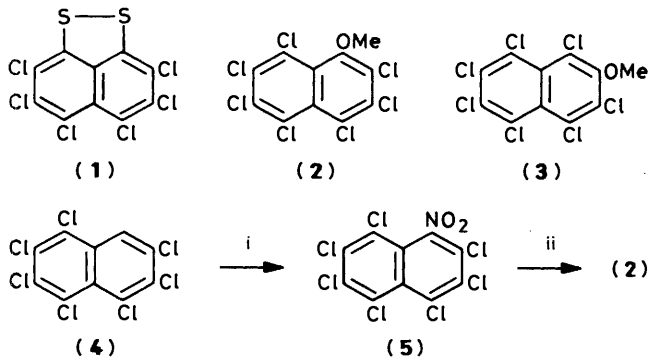
Octachloronaphthalene is substituted by methoxide predominantly at the α-position; it is reduced by lithium aluminium hydride or by phenylhydrazine to give 1*H*-heptachloronaphthalene. 1*H*-Heptachloronaphthalene has been nitrated to give heptachloro-8-nitronaphthalene, which has been used to make heptachloro-8-methoxynaphthalene, heptachloro-1-naphthylamine, and 1-bromoheptachloronaphthalene.

Although octachloronaphthalene has been known for over a century,[2] and was the major component of a commercially available material,[3] very little has been published concerning its chemistry.[4] In particular, in contrast to analogues such as hexachlorobenzene[4,5] and octafluoronaphthalene[6] almost nothing has been published concerning its reactions with nucleophiles. The only reports of nucleophilic substitution concern the reduction to 1*H*-heptachloronaphthalene with lithium aluminium hydride,†[7] the interesting reaction with disulphide giving the heterocyclic compound (**1**) (and related reactions with selenium and tellurium),[9] and reaction with hydroxide ion.[10] It is noteworthy that in all these cases 1-substitution was reported,‡ whereas in the case of octafluoronaphthalene, 2-substitution is the rule.[6]

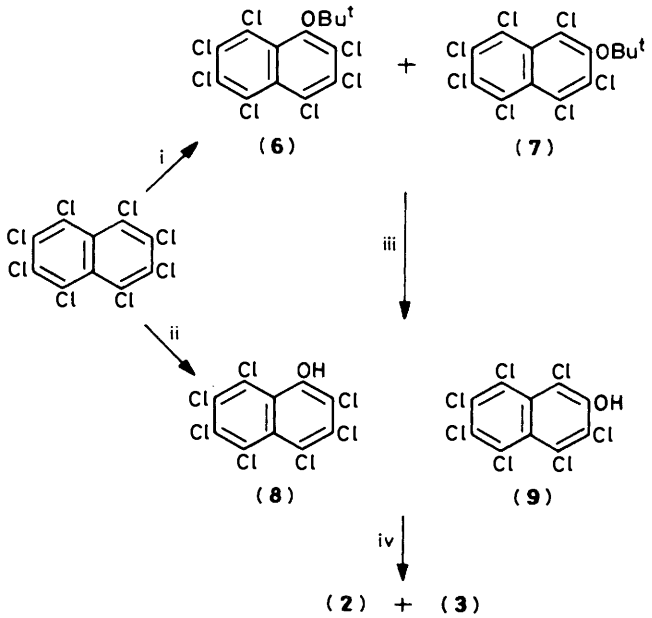
Preliminary investigations of the reactions of octachloronaphthalene with alkoxides and amines revealed the reason for the lack of published results, since under conditions suitable for analogous substrates only tars were obtained. Nevertheless, under carefully controlled conditions, identifiable products were obtained with certain reagents. For example, when octachloronaphthalene was treated under reflux with sodium methoxide in pyridine for a few minutes, a mixture of heptachloromethoxy-, hexachlorodimethoxy-, and pentachlorotrimethoxy-naphthalenes was obtained. The mono-, di-, and trimethoxy derivatives could be separated from each other, but only one of the monomethoxy compounds was obtained pure, and the di- and tri-methoxy compounds remain uncharacterised.

In order to distinguish between the two possible heptachloromethoxynaphthalenes (**2**) and (**3**), the 1(8)-methoxy isomer (**2**) was synthesised independently from 1*H*-heptachloronaphthalene (**4**) as shown in Scheme 1.

Nitration of the heptachloronaphthalene with nitric acid resulted in extensive oxidation giving quinones (*cf.* ref. 11), but nitronium tetrafluoroborate gave heptachloro-8-nitronaphthalene (**5**) cleanly (*cf.* ref. 12). Reaction with sodium methoxide in acetonitrile then proceeded mainly by displacement of the nitro group, giving heptachloro-8-methoxynaphthalene (**2**) (*cf.* ref. 13). This compound (**2**) proved to be identical with the major monomethoxy compound from the reaction of sodium methoxide with octachloronaphthalene. Compound (**2**) was also used to identify the products from the reactions of octachloronaphthalene with t-butoxide[1] and hydroxide,[10] as summarised in Scheme 2. The mixture of t-butoxyheptachloronaphthalenes (**6**) and (**7**)[1] was cleaved with



Scheme 1. *Reagents:* i, NO_2BF_4; ii, NaOMe

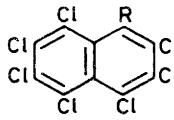


Scheme 2. *Reagents:* i, Bu^tOK, THF; ii, KOH, Me_2SO; iii, H_3O^+; iv, KOH, Me_2SO_4

acid, and the resulting mixture of naphthols (**8**) and (**9**) was methylated, to give a mixture of the 8- (**2**) and 7-methoxy (**3**) compounds in the ratio *ca.* 85:15. On the other hand, methylation of the product from a reaction of octachloro-

† The identity of the product has since been confirmed.[8]

‡ In the last case, no evidence was given; see below for further discussion.



(10) R = NH_2
(11) R = Br

naphthalene with potassium hydroxide in dimethyl sulphoxide gave a mixture of the 8- (2) and 7-methoxy (3) compounds in the ratio *ca.* 30:70, in contrast to the reported α-substitution (the yields were, however, poor). Since our work was completed, it has been reported that dechlorination of octachloronaphthalene by sodium naphthalene in tetrahydrofuran (THF) was accompanied by nucleophilic substitution by adventitious hydroxide ion, but the position of substitution was not determined.[14]

Reactions of octachloronaphthalene with sodium ethoxide in pyridine gave mixtures of polysubstituted products, none of which has been characterised. Reactions with piperidine under a variety of conditions gave only starting material and/or tar. Hydrazine hydrate failed to react with octachlorophthalene, but a reaction with phenylhydrazine in dimethylformamide (DMF) proceeded by *reduction* rather than substitution, giving 1*H*-heptachloronapthalene (4) in high yield. In the latter case, the reaction mixture became highly coloured, and we suggest that an electron-transfer process may be involved.

In general, our results confirm that octachloronaphthalene undergoes nucleophilic substitution at an α-position, in contrast to octafluoronaphthalene. It is difficult to explain the difference in electronic terms (though the possibility of electron-transfer processes[15] should be considered). However, steric factors may be predominant in the case of naphthalene, where the severe interaction between *peri*-chlorine atoms[16] would be relieved in going to a Meisenheimer-type intermediate.

Heptachloro-8-nitronaphthalene (5) is a useful intermediate for preparing further heptachloronaphthyl derivatives. We have reduced it to the naphthylamine (10), and thence by a Sandmeyer reaction synthesised the bromoheptachloronaphthalene (11). The nitronaphthalene (5) could not, however, be used to prepare secondary amino derivatives directly, since reaction with piperidine, for example, gave an *N*-hexachloronitronaphthylpiperidine.

Experimental

N.m.r. spectra were recorded at 90 MHz in $CDCl_3$ with Me_4Si as internal standard. Mass spectral data are given for ions containing ^{35}Cl and/or ^{79}Br only; appropriate isotopic clusters were observed. Chromatography was on silica, using gradient elution with chloroform in light petroleum, b.p. 60–80 °C, unless otherwise stated. Octachloronaphthalene was obtained from Halowax 1051.[3,7]

Reactions of Octachloronaphthalene.—(*a*) *With sodium methoxide.* (i) A solution of sodium hydroxide (1.0 g) in hot methanol (25 ml) was added quickly with vigorous stirring to a boiling solution of octachloronaphthalene (8.0 g) in pyridine (100 ml). The mixture was heated under reflux for 10 min, cooled, and filtered. The filtrate was poured onto ice, and the resulting precipitate was recovered by filtration and dissolved in diethyl ether. The solution was dried ($MgSO_4$) and evaporated. Chromatography of the residue (eluant light petroleum) gave (a) a mixture of heptachloro-7-methoxynaphthalene and (mainly) heptachloro-8-methoxynaphthalene (2.3 g, 25%), m.p. 137—140 °C; δ 4.0 (s) and 3.90 (s) integration ratio *ca.* 1:10 (Found: C, 33.4; H, 0.9%; M^+, 395.8000. Calc. for $C_{11}H_3Cl_7O$: C, 33.2; H, 0.8%; M^+, 395.8005); (b) hexachlorodimethoxynaphthalene(s) (2.2 g, 25%), m.p. 255—256 °C; δ 3.95 (s) and 4.15 (s) (Found: C, 36.8; H, 1.5%; M^+, 391.8496. Calc. for $C_{12}H_6Cl_6O_2$: C, 36.5; H, 1.5%; M^+, 391.8504); and (c) pentachlorotrimethoxynaphthalene(s) (1.7 g, 20%), m.p. 170—172 °C; δ 3.9 (s), 4.0 (s), and 5.0 (s) (Found: C, 39.7; H, 2.1%; M^+, 387.8992. Calc. for $C_{13}H_9Cl_5O_3$: C, 40.0; H, 2.1%; M^+, 387.9007).

(ii) A solution of sodium hydroxide (0.4 g) in methanol (10 ml) was added to a boiling solution of octachloronaphthalene (4.0 g) in pyridine (100 ml), and the mixture was heated under reflux for 10 min. The mixture was poured into ice–water (100 ml) and the resulting precipitate was recovered by filtration. Chromatography followed by recrystallisation from light petroleum gave heptachloro-8-methoxynaphthalene (2) (2.5 g, 63%), identical with the material obtained from heptachloro-8-nitronaphthalene described below, and mixtures of hexachlorodimethoxy- and pentachlorotrimethoxy-naphthalenes.

(*b*) *With sodium ethoxide.* An experiment similar to the experiment described above, but with ethanol in place of methanol, gave (i) hexachlorodiethoxynaphthalene(s) (2.7 g, 30%), m.p. 179—180 °C; δ 4.1 (4 H, q) and 1.6 (6 H, t) (Found: C, 39.7; H, 2.1. Calc. for $C_{14}H_{10}Cl_6O_2$: C, 39.7; H, 2.3%); and (ii) (eluted with tetrachloromethane) a mixture (3.0 g), m.p. *ca.* 200 °C, of hexachlorodi- and pentachlorotri-ethoxynaphthalenes.

(*c*) *With potassium hydroxide.* To a solution of potassium hydroxide (5 g) in water (5 ml) was added, with stirring, hot (100 °C) dimethyl sulphoxide (200 ml). The solution was heated to 120 °C and octachloronaphthalene (8.0 g) was added. The mixture was maintained at 120 °C for 20 min, and then allowed to cool. Water (50 ml) and conc. hydrochloric acid (100 ml) were added and the precipitate (7.1 g) was recovered by filtration. A portion of the precipitate (1.0 g) was heated under reflux with anhydrous potassium carbonate (2.0 g) and dimethyl sulphate (5.0 ml) in acetone (25 ml) for 1 h. The mixture was cooled, added to 20% aqueous ammonium hydroxide, and extracted with chloroform (3 × 50 ml). The extract was dried ($MgSO_4$) and evaporated to dryness. Chromatography of the residue gave a mixture (0.2 g) of heptachloro-8-methoxynaphthalene (δ 3.9) and heptachloro-7-methoxynaphthalene (δ 4.0) in the ratio of *ca.* 1:2.3 (by n.m.r.).

(*d*) *With lithium aluminium hydride.* Octachloronaphthalene (8.0 g, 20 mmol) was heated under reflux with lithium aluminium hydride (0.4 g, 20 mmol) in tetrahydrofuran (100 ml) for 4 h. Hydrolysis with water (20 ml) and 4M-sulphuric acid (10 ml) followed by conventional work-up and chromatography (silica, light petroleum) gave 1*H*-heptachloronaphthalene (4) (4.8 g, 60%), m.p. 160—162 °C, identical (n.m.r., i.r.) with a sample prepared by a Ponomarenko reaction on 1,2,3,4,5,6-hexachloro-7-nitronaphthalene.[8a]

(*e*) *With piperidine.* No reaction was observed between octachloronaphthalene and piperidine in boiling toluene or pyridine; in sulpholane at 200 °C, starting material and tar were obtained; with piperidine as solvent in a Carius tube at 170 °C for 4 h, a black, sticky, rubbery product was obtained, from which no pure compounds could be isolated, but which contained (^1H n.m.r.) piperidino groups.

(*f*) *With hydrazine hydrate.* No reaction was observed between octachloronaphthalene and hydrazine hydrate in ethanol, toluene, or dimethyl formamide.

(*g*) *With phenylhydrazine.* Octachloronaphthalene (4 g, 10 mmol), phenylhydrazine (1.08 g, 10 mmol), anhydrous potassium carbonate (1.38 g, 10 mmol), and DMF (100 ml) were heated under reflux for 4 h. The black mixture was cooled and added to saturated aqueous sodium chloride, and the resulting precipitate was recovered by filtration. Recrystallisation (tetrachloromethane–toluene) gave 1*H*-heptachloronaphthalene (4) (2.9 g, 80%), identical with the material obtained by reduction of octachloronaphthalene by lithium aluminium hydride.

A similar result was obtained when the reaction time was reduced to 10 min.

Identification of t-Butoxyheptachloronaphthalenes.—To the product from the reaction of octachloronaphthalene (1.0 g) with potassium t-butoxide in THF[1] was added at room temperature conc. hydrochloric acid (5 ml) and the mixture was stirred for 10 min. The solvent was evaporated under reduced pressure and the residue was dissolved in 10% aqueous potassium hydroxide. Dimethyl sulphate (5 ml) was added, and the mixture was heated under reflux for 1 h. Work-up as described for the reaction of octachloronaphthalene with potassium hydroxide gave a mixture (0.3 g) of heptachloro-8-methoxynaphthalene (δ 3.9) and heptachloro-7-methoxynaphthalene (δ 4.0) in the ratio of *ca.* 85:15 (by n.m.r.).

Octachloro-8-nitronaphthalene (**5**).—A mixture of 1*H*-heptachloronaphthalene (2.0 g, 5.5 mmol), nitronium tetrafluoroborate (1.4 g, 10 mmol), and sulpholane (15 ml) was heated at 70 °C for 8 h. Water (100 ml) was added, and the resulting yellow precipitate was recovered by filtration and recrystallised from propan-2-ol–toluene to give *heptachloro-8-nitronaphthalene* (**5**) (1.3 g, 57%), m.p. 168—170 °C (Found: C, 29.1; N, 3.3%; M^+, 411. $C_{10}Cl_7NO_2$ requires C, 29.0; N, 3.4%; M^+, 411).

Reactions of Heptachloro-8-nitronaphthalene.—(*a*) *With sodium methoxide.* To a solution of heptachloro-8-nitronaphthalene (0.50 g, 1.2 mmol) in acetonitrile (50 ml) was added a solution of sodium methoxide (0.07 g, 1.2 mmol) in methanol (0.7 ml) and the resulting solution was heated under reflux for 1 h and cooled. Water (30 ml) was added, the mixture was filtered, and the precipitate subjected to chromatography which gave (i) *heptachloro-8-methoxynaphthalene* (0.27 g, 56%), m.p. 137—140 °C; δ 3.9 (s) (Found: C, 33.0; H, 0.8%; M^+, 396. $C_{11}H_3Cl_7O$ requires C, 33.0; H, 0.8%; M^+, 396); and (ii) mixtures of polymethoxylated chloro- and chloronitro-naphthalenes.

(*b*) *With piperidine.* Piperidine (0.12 ml, 1.2 mmol) was added to a solution of heptachloro-8-nitronaphthalene (0.5 g, 1.2 mmol) in acetonitrile (30 ml) containing anhydrous potassium carbonate (0.5 g). The mixture was heated under reflux for 90 min. Conventional work-up, followed by chromatography, gave yellow *N*-hexachloronitronaphthylpiperidine (0.25 g, 44%), m.p. 110—112 °C (from ethanol); δ 1.7br (6 H) and 3.2br (4 H) (Found: C, 39.0; H, 2.2; N, 5.9%; M^+, 460. Calc. for $C_{15}H_{10}Cl_6N_2O_2$: C, 38.9; H, 2.2; N, 6.05%; M^+, 460).

(*c*) *Reduction.* A solution of heptachloro-8-nitronaphthalene (1.0 g) in toluene containing 5% palladium on charcoal (0.1 g) was shaken under hydrogen for 24 h, during which time 120 ml were absorbed. The reaction mixture was filtered through Kieselguhr and evaporated to dryness. Chromatography of the residue gave (i) heptachloro-8-nitronaphthalene (0.2 g, 20%) and (ii) *heptachloro-1-naphthylamine* (**10**) (0.65 g, 70%), m.p. 180—182 °C; $\nu_{max.}$ 3 400, 3 500 cm^{-1} (i.r. spectrum identical with that recorded by Beck[17]) (Found: C, 32.0; H, 0.7; N, 4.1%; M^+, 381. $C_{10}H_2Cl_7N$ requires C, 31.25; H, 0.5; N, 3.6%; M^+, 381).

(*d*) *1-Bromoheptachloronaphthalene.* A suspension of heptachloro-1-naphthylamine (1.0 g) in conc. sulphuric acid (30 ml) was kept below 10 °C as sodium nitrite (0.25 g) was added, and the mixture was stirred for 10 min. The mixture was added to ice–water (10 ml) and the resulting bright yellow suspension was added to a solution of copper(I) bromide in conc. hydrobromic acid. The mixture was heated under reflux for 1 h, cooled, diluted with water (50 ml), and neutralised with 10% aqueous sodium hydroxide. Work-up *via* extraction with toluene and chromatography gave *1-bromoheptachloronaphthalene* (**11**) (0.55 g, 47%), m.p. 203—205 °C (Found: 26.7%; M^+, 444. $C_{10}BrCl_7$ requires C, 26.8%; M^+, 444).

Acknowledgements

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