# Aryne Chemistry. Part XXXVI.[1] Approaches to the Synthesis of 5,6,7,8-Tetrahalogeno-1,4-dihydro-2-nitroso-1,4-ethenonaphthalenes (2-Nitroso-tetrahalogenobenzobarrelenes)

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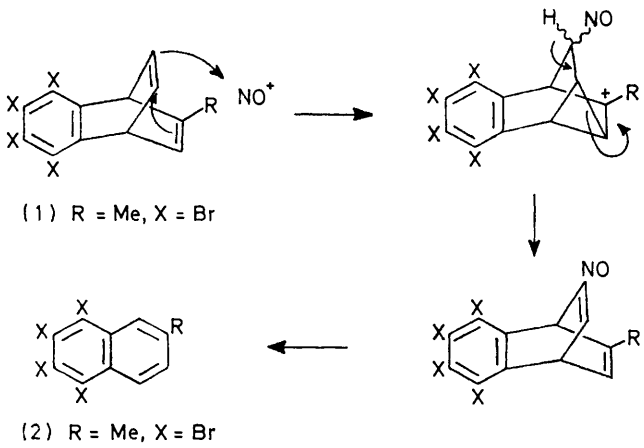
The reactions of arynes, generated by aprotic diazotisation of the corresponding anthranilic acids, with nitrosoarenes gave *N*-hydroxycarbazole derivatives. 1,4-Dihydro-2-nitroso-1,4-ethenonaphthalene derivatives were implicated in reactions of 3-bromo-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one oximes with triethylamine, which led to the expected naphthalene derivatives.

DURING earlier work [2] we showed that the aprotic diazotisation of tetrabromoanthranilic acid in certain alkylbenzenes led to the formation of alkyltetrabromonaphthalenes. Thus, for example, in the presence of toluene we obtained 1,2,3,4-tetrabromo-6-methylnaphthalene (2) in addition to the expected products. It was also shown that the naphthalene (2) arose from 5,6,7,8-tetrabromo-1,4-dihydro-2-methyl-1,4-ethenonaphthalene (2-methyltetrabromobenzobarrelene) (1).

The conversion of benzobarrelene derivatives into naphthalenes by retro-Diels–Alder reactions is well known,[3] but these reactions normally proceed only at temperatures around 400°. Furthermore the acetylene which is lost preferentially is normally the most substituted. We tentatively suggested a mechanism involving attack by the nitrosonium ion and formation of a nitrosobenzobarrelene.[2]

We have now verified the involvement of the nitrosonium ion by obtaining low yields of the naphthalene (2) from the benzobarrelene derivative (1) in the presence of various nitrosating agents (Scheme 1). Whereas the decomposition of the benzobarrelene (1) was only complete after *ca.* 3 days when pentyl nitrite was used at 80°, when we used nitrosyl chloride reaction was rapid, and with trifluoroacetyl nitrite reaction was instantaneous at room temperature. The yield of the naphthalene (2) varied from 4 to 17% and was lowest when the most powerful nitrosating agent was used. Although the naphthalene derivatives were isolated without difficulty, none of the other products were identified. They were very polar [4] and could not be resolved by t.l.c.

The disproportionation reaction was not observed with the parent tetrahalogenobenzobarrelenes or with, for example, the adduct of tetrabromobenzyne with *p*-xylene. This suggested that the attack on a disubstituted double bond required the presence of an alkyl group (or alkyl groups) on the homoconjugated double bond in order to stabilise the cationic centre (Scheme 1). The formation of similar cations, as a result of homoconjugation in benzobarellenes, has been suggested previously.[5] The stabilisation of the carbocation is presumably sufficient to allow some proton loss rather than complete scavenging by nucleophiles. Deprotonation of the carbocation would give a nitrosobenzobarrelene, which would afford the naphthalene and nitrosoacetylene. Unsaturated nitroso-compounds,




SCHEME 1

other than nitrosoarenes, are not well known [6] and as far as we are aware 1-nitrosohex-1-yne and 3,3-dimethyl-1-nitrosobut-1-yne are the only examples of their type to be well established.[7]

We studied two approaches to the synthesis of 2-nitrosobenzobarrelenes. The cycloaddition reaction of benzyne with nitrosobenzene has been reported to afford *N*-phenylcarbazole.[8] However, many reactions of the tetrahalogenobenzynes with substituted arenes result in cycloaddition to the arene residue.[9] It was hoped that the presence of electron-releasing substituents on the arene residue would facilitate such cycloadditions. We carried out a number of reactions of nitrosoarenes with both tetrabromo- and tetrachloro-benzyne and in each

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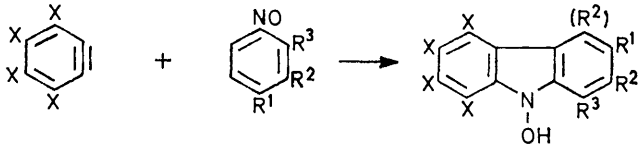
case we isolated the corresponding *N*-hydroxycarbazole (Scheme 2). In the previous report of the reaction of



(3) X = H, $R^1 = R^2 = R^3 = H$
(4) X = Cl, $R^1 = R^2 = R^3 = H$
(5) X = Br, $R^1 = R^2 = R^3 = H$
(6) X = Br, $R^1$ = Me, $R^2 = R^3 = H$
(7) X = Br, $R^1$ = OMe, $R^2 = R^3 = H$
(8) X = Br, $R^1 = R^2 = H$, $R^3$ = OMe
(9) X = Br, $R^1 = R^3 = H$, $R^2$ = Me

SCHEME 2

benzyne with nitrosobenzene the benzyne was generated from benzothiadiazole 1,1-dioxide. We generated the arynes from arenediazonium-2-carboxylates and also obtained *N*-hydroxycarbazole (3) in very low yield from the reaction of benzyne with nitrosobenzene. The isolated yields of *N*-hydroxycarbazoles in reactions with tetrahalogenobenzynes ranged from 9 to 30%. No naphthalene derivatives were detected. No products were isolated from an attempted reaction between tetrachlorobenzyne and nitrosomesitylene. The structures of the *N*-hydroxycarbazoles (4)—(9) were proved by elemental analysis and spectroscopic methods, and in the case of the compound (5) by conversion into the *N*-methoxy-derivative.

The second approach to the preparation of nitrosobenzobarrelenes involved the dehydrobromination of α-bromo-oximes. 1-Nitrosocyclohexene has recently been prepared in this way from 2-chlorocyclohexanone.[10] We were unable to brominate tetrabromo- or tetrachloro-benzobarrelenone with either *N*-bromosuccinimide naphthalene derivatives (14) and (15) in 38 and 47% yields, respectively.

These results clearly implicate the intermediacy of nitrosobenzobarrelene derivatives. But nitrosoacetylene has remained undetected even in the presence of thebaine, which is well known as a good substrate both for conventional dienophiles and for *C*-nitroso-compounds.[12] Thus the presence of electron-withdrawing 2-substituents in benzobarrelene derivatives leads to their ready fragmentation.

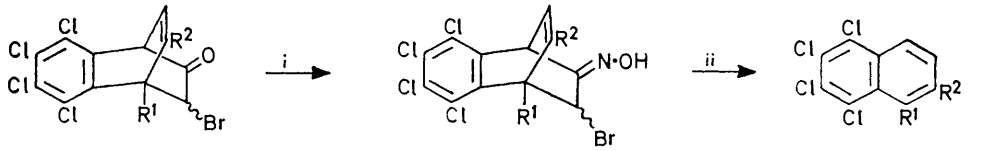
## EXPERIMENTAL

The general methods used are given in ref. 11.

*Reactions of 5,6,7,8-Tetrabromo-1,4-dihydro-2-methyl-1,4-ethenonaphthalene* (1) *with Nitrosating Agents.*—(a) *Pentyl nitrite.* The ethenonaphthalene (1) [2] (500 mg) and pentyl nitrite (1 ml) were dissolved in benzene (10 ml) and stirred at 60°, and acetic acid (5 drops) was added. After 16 h t.l.c. indicated the presence of starting material, and more pentyl nitrite (1 ml) and acetic acid (5 drops) were added. The reaction was monitored by t.l.c. and after 3 days no starting material was detected. The solution was washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The residue was placed on a column of silica gel; elution with light petroleum gave 1,2,3,4-tetrabromo-6-methylnaphthalene (2) (80 mg, 17%), m.p. and mixed m.p. 120—122° (lit.,[2] 121°), identical (i.r., u.v., and $^1$H n.m.r. spectra) with authentic material.[2] Further elution with more polar solvents gave unidentified oils.

(b) *Nitrosyl chloride.* The ethenonaphthalene (1) (50 mg) in carbon tetrachloride (30 ml) was treated with nitrosyl chloride (*ca.* 0·1 g) and the solution was stirred at room temperature for 30 h. Conventional work-up and preparative layer chromatography gave 1,2,3,4-tetrabromo-6-methylnaphthalene (2) (4 mg, 8%), identical with the material described in (a).

(c) *Trifluoroacetyl nitrite.*[13] The ethenonaphthalene (1) (500 mg) was dissolved in carbon tetrachloride (10 ml) at room temperature and trifluoroacetyl nitrite (200 mg) was added. An instantaneous green colour was produced and



(10) $R^1$ = H, $R^2$ = Me
(11) $R^1$ = OMe, $R^2$ = H
(12) $R^1$ = H, $R^2$ = Me
(13) $R^1$ = OMe, $R^2$ = H
(14) $R^1$ = H, $R^2$ = Me
(15) $R^1$ = OMe, $R^2$ = H

SCHEME 3 Reagents: i, $HONH_3^+Cl^-$; ii, $Et_3N$–$Me_2NCHO$

or dimethyl dibromohydantoin. However, 3-bromo-5,6,7,8-tetrahalogeno-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one derivatives are available from the reactions of tetrahalogenobenzynes with suitable 2-bromoanisole derivatives.[11] The ketones (10) and (11) were converted into the corresponding oximes (12) and (13), which were heated at *ca.* 100° in dimethylformamide in the presence of triethylamine and afforded the the solvent was removed. The residue was triturated with light petroleum and the insoluble material was removed. Preparative layer chromatography gave 1,2,3,4-tetrabromo-6-methylnaphthalene (2), identical with the material described in (a) (19 mg, 4%). The fraction insoluble in light petroleum showed almost no $^1$H n.m.r. absorption, and attempts to isolate further products from the light-petroleum-soluble fraction were unsuccessful.

*Reactions of Arynes with Nitrosoarenes.*—(a) *Tetrabromobenzyne with nitrosobenzene.* Tetrabromoanthranilic acid [2]

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[13] D. E. Rice and G. H. Crawford, *J. Org. Chem.*, 1963, **28**, 872.

(4·56 g, 0·01 mol) in acetonitrile (170 ml) was added concurrently with a solution of pentyl nitrite (1·36 ml, 0·01 mol) in acetonitrile (170 ml), during 45 min, to a solution of nitrosobenzene (4·3 g, 0·04 mol) in acetonitrile (50 ml) which was maintained at 50—55°. The stirred solution was maintained at 50—55° for a further 45 min, the solvent was removed, and the residue was placed on a column of neutral alumina (activity I; 100 g). Elution with benzene–light petroleum (1 : 1) gave (*a*) azoxybenzene (220 mg) and (*b*) nitrosobenzene (420 mg). Elution with benzene gave, as a pale yellow solid, 2,3,4,5-*tetrabromo*-N-*hydroxycarbazole* (5) (1·27 g, 25%), m.p. 216—217° (from benzene–light petroleum) (Found: C, 28·95; H, 1·1; N, 2·5%; $M^{+\cdot}$, 499. $C_{12}H_5Br_4NO$ requires C, 28·9; H, 1·0; N, 2·8%; *M*, 499); τ −1·90 (1H, s, exchangeable), 1·32—1·55 (1H, m), and 2·20—2·87 (3H, m); $\nu_{max.}$ (KBr) 3425 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 222 (log ε 4·58), 250 (4·72), 260 (4·67), 272 (4·54), 295 (4·13), 304 (4·17), 339 (3·75), and 352 (3·78) nm.

A sample of compound (5) (250 mg) in dimethyl sulphoxide (40 ml) was stirred with a suspension of potassium hydroxide (100 mg) and methyl iodide (200 mg) at room temperature during 16 h. Water (200 ml) was added; the precipitate gave 2,3,4,5-*tetrabromo*-N-*methoxycarbazole* (105 mg, 41%), m.p. 170—172° (from benzene–methanol (Found: C, 30·75; H, 1·5; N, 2·75%; $M^{+\cdot}$, 513. $C_{13}H_7Br_4NO$ requires C, 30·45; H, 1·4; N, 2·75%; *M*, 513); τ 1·20—1·43 (1H, m), 2·43—2·90 (3H, m), and 5·90 (3H, s); $\lambda_{max.}$ (EtOH) 224 (log ε 4·48), 253 (4·59), 263 (4·58), 272 (4·53), 297 (4·06), 304 (4·05), 347 (3·66), and 360 (3·70) nm.

(b) *Tetrachlorobenzyne with nitrosobenzene.* By an analogous procedure this gave 2,3,4,5-*tetrachloro*-N-*hydroxycarbazole* (4) (20%), m.p. 174—175° (from benzene–light petroleum) (Found: C, 44·75; H, 1·65; N, 4·35%; $M^{+\cdot}$, 321. $C_{12}H_5Cl_4NO$ requires C, 44·9; H, 1·55; N, 4·35%; *M*, 321); τ 1·50—1·80 (1H, m) and 2·25—2·90 (3H, m); $\nu_{max.}$ (KBr) 3450 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 248 (log ε 4·54), 255 (4·48), 265 (4·33), 302 (4·01), 337 (3·62), and 350 (3·50) nm.

(c) *Benzyne with nitrosobenzene.* By an analogous procedure this gave N-*hydroxycarbazole* (3) (1%), m.p. 219—220° (from benzene–light petroleum) (Found: C, 79·15; H, 5·05; N, 7·75%; $M^{+\cdot}$, 181. $C_{12}H_9NO$ requires C, 78·65; H, 4·9; N, 7·6%; *M*, 181); τ 1·70—2·00 (2H, m) and 2·30—3·00 (6H, m); $\nu_{max.}$ (KBr) 3430 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 233 (log ε 4·65), 244 (4·41), 257 (4·33), 293 (4·26), 324 (3·65), and 337 (3·61) nm.

(d) *Tetrabromobenzyne with* p-*nitrosotoluene.*[14] This gave 2,3,4,5-*tetrabromo*-N-*hydroxy*-7-*methylcarbazole* (6) (29%), m.p. 219—221° (from methanol) (Found: C, 30·7; H, 1·5; N, 2·7%; $M^{+\cdot}$, 513. $C_{13}H_7Br_4NO$ requires C, 30·45; H, 1·4; N, 2·75%; *M*, 513); *m/e* 492·7305 (*M* − 16; $C_{13}H_7{}^{79}Br_4N$ requires 492·7295); τ 1·72br (1H, s), 1·59br (2H, q, |*J*| 8·9 Hz), and 7·55 (3H, s); $\nu_{max.}$ (KBr) 3460 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 223 (log ε 4·63), 250 (4·76), 263 (4·72), 270 (4·60), 298 (4·21), 307 (4·23), 344 (3·78), and 360 (3·80) nm.

(e) *Tetrabromobenzyne with* p-*nitrosoanisole.*[15] This gave 2,3,4,5-*tetrabromo*-N-*hydroxy*-7-*methoxycarbazole* (7) (13%), m.p. 237—238° (from benzene–light petroleum) (Found: C, 30·2; H, 1·2; N, 2·7%; $M^{+\cdot}$, 529. $C_{13}H_7Br_4NO_2$ requires C, 29·5; H, 1·35; N, 2·65%; *M*, 529); τ 1·1br (1H, s, exchangeable) 2·00 (1H, d, |*J*| 2·7 Hz), 2·45 (1H, d, |*J*| 8·2 Hz), 2·80 (1H, q, |*J*| 8·2 and 2·7 Hz), and 6·17 (3H, s); $\nu_{max.}$ (KBr) 3450 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 246 (log ε 4·24), 256 (4·21), 266 (4·20), 277 (4·17), 311 (3·80), and 365 (3·39) nm.

(f) *Tetrabromobenzyne with* o-*nitrosoanisole.*[14] This gave 2,3,4,5-*tetrabromo*-N-*hydroxy*-9-*methoxycarbazole* (8) (16%), m.p. 198—201° (from benzene–light petroleum) (Found: C, 29·55; H, 1·3; N, 2·6%; $M^{+\cdot}$, 529); τ 1·82 (1H, q, |*J*| 6·8 and 2·7 Hz), 2·58—2·95 (2H, m), and 6·00 (3H, s); $\nu_{max.}$ (KBr) 3460 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 230 (log ε 4·70), 252 (4·78), 293 (4·07), and 343 (3·81) nm.

(g) *Tetrabromobenzyne with* m-*nitrosotoluene.*[14] This gave a mixture of 2,3,4,5-tetrabromo-*N*-hydroxy-6-methyl- and -8-methyl-carbazoles (9) (9%), τ 6·95 and 7·50 (Me) in the ratio 2 : 1.

*Preparation of* 1,2,3,4-*Tetrachloro*-6-*methylnaphthalene from* 3-*Bromo*-5,6,7,8-*tetrachloro*-3,4-*dihydro*-9-*methyl*-1,4-*ethenonaphthalen*-2(1H)-*one* (10).—The ketone (10)[11] (400 mg) and hydroxylamine hydrochloride (200 mg) were dissolved in pyridine (25 ml), heated at 80° for 2 h, and poured into ice–water (200 ml). The precipitate gave the *oxime* (12) (330 mg, 79%), m.p. 202—203° (from benzene–methanol) (Found: C, 37·65; H, 2·0; N, 3·3%; $M^{+\cdot}$, 415. $C_{13}H_8BrCl_4NO$ required C, 37·55; H, 1·5; N, 3·35%; *M*, 416).

The oxime (12) (300 mg) was heated in dimethylformamide (20 ml) and triethylamine (1 ml) at *ca.* 100° for 3 h. The solution was evaporated *in vacuo* and the residue was purified by preparative layer chromatography, giving a lower band of unchanged oxime (99 mg) and an upper band of 1,2,3,4-tetrachloro-6-methylnaphthalene (14) (65 mg, 38%), m.p. and mixed m.p. 125—127° (from ethanol), identical (u.v., i.r., and $^1H$ n.m.r. spectra) with an authentic sample.[11]

*Preparation of* 1,2,3,4-*Tetrachloro*-5-*methoxynaphthalene from* 3-*Bromo*-5,6,7,8-*tetrachloro*-3,4-*dihydro*-4-*methoxy*-1,4-*ethenonaphthalen*-2(1H)-*one* (11).—By an analogous procedure the ketone (11) was converted into the oxime (13) and thence into 1,2,3,4-tetrachloro-5-methoxynaphthalene (15) (47%), m.p. and mixed m.p. 134—136° (from ethanol), identical (u.v., i.r., and $^1H$ n.m.r. spectra) with an authentic sample.[11]

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