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The Dechlorination of Some Highly Chlorinated Naphthalene Derivatives

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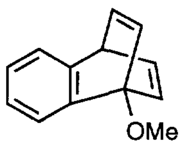
Abstract: *The [4+2] cycloadducts formed between tetrachlorobenzyne and a variety of arenes and cyclic 1,3-dienes have been reductively dechlorinated. The products are formally benzyne cycloadducts, many of which are difficult to make by other routes. High yields are obtained when sodium and t-butanol in boiling THF are used for the reduction. THF serves as a solvent but t-butanol not only acts as a proton donor but also appears to initiate the reduction. Tetrachlorobenzyne should be considered as an alternative reagent whenever benzyne itself appears to be required.*

Introduction

We[1] and others[1a,2] have previously described the cycloaddition reactions of tetrachlorobenzyne with a variety of cyclic dienes. The procedure permits the rapid construction of a number of carbocyclic systems that are not easily accessible by other routes. Tetrachlorobenzyne nearly always offers synthetic advantages over benzyne itself:[1a,3] its reactions often proceed in higher yield; it is readily available from inexpensive precursors - the convenient diazotised-tetrachloroanthranilic acid is less hazardous than diazotised anthranilic acid itself; the products are in general more easily isolated and purified; and the aromatic ring is protected against attack -e.g. sulphonation - during subsequent steps. However, the number of times that a tetrachlorobenzannulated product might be a synthetic target *per se* is limited. When we required derivatives of 1-methoxy-1,4-dihydro-1,4-ethenonaphthalene (1-methoxybenzobarrelene) (**1**) for our studies[4] of the acid-catalysed rearrangements of this ring system we decided to tackle our specific problem by solving a long-standing problem of more general concern. The analogy between tetrachlorobenzyne and other perchlorinated reactive intermediates such as dichlorocarbene[5] or dichloroketene[6] is clear. What is required is a straightforward reductive dechlorination procedure that can be applied to tetrachlorobenzyne adducts.



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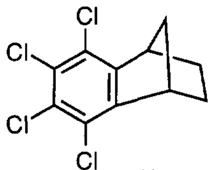

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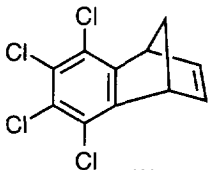

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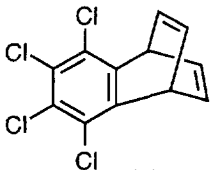

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The dehalogenation of aromatic rings has frequently been reported. Wilt has reported[7] reductive dechlorination of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-1,4-methanonaphthalenes (tetrachlorobenzonorbornenes) (**2**) with Raney nickel alloy and potassium hydroxide: reduction of double bonds would undoubtedly complicate our use of this reagent. An apparently better procedure is that of Bruck[8] in which tetrachlorobenzonorbornadiene (**3**) is reduced by lithium and *t*-butanol in tetrahydrofuran at reflux; in this procedure some amount of over-reduction to benzonorbornene also occurred. Gassman[9] has modified this procedure to minimise double bond reduction in a different context by substituting sodium for lithium. The use of sodium and *t*-butanol for reductive dechlorination is more generally widespread[10] so we chose to adapt Gassman's modified procedure to the reductive dechlorination of the adducts formed from tetrachlorobenzyne and arenes. We have developed a simple procedure to effect the necessary *tetrakis*-hydrodechlorination in remarkably high yield and we now describe full details of the comparative advantage, scope, and mechanism of this reaction.

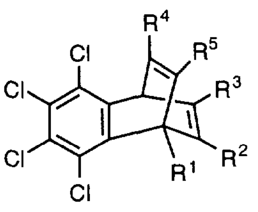
Results and Discussion

The advantages of tetrachlorobenzyne over benzyne itself are clearest in its reactions with aromatic systems.[1a] We therefore studied the reductive dechlorination of the major classes of cycloadduct formed from tetrachlorobenzyne and arenes. The cycloadducts formed most commonly[1a] in this way are derivatives of 5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene (tetrachlorobenzobarrelene) (**4**). We chose tetrachlorobenzobarrelene (**4**)[11] as a model for most of our work on the optimisation of reaction conditions. The majority of the tetrachlorobenzobarrelene derivatives studied have already been reported. Additional compounds (see Table 1) were prepared from pentachlorophenyllithium and the appropriate aromatic compound.

After some experimentation, in which reagent and solvent ratios and reaction time and temperature were varied, we selected a substrate:sodium:*t*-butanol:tetrahydrofuran ratio of *ca.* 1:1:3:40 by weight at reflux temperature as conditions that would give very nearly quantitative yields within 24 hours.[3] Remarkably, no reduction was detected even after 50 hours in a similar reaction conducted at 0-5 °C. Under our preferred conditions the end of the reduction is indicated when the precipitate of sodium chloride turns deep purple.

Similar reductions were attempted with sodium-biphenyl-glyme,[12] magnesium-*i*-propanol-decalin,[13] and potassium hydroxide-Raney nickel alloy[7] with no or little success. Reductive dechlorination using hydrazine hydrate[14] in the presence of palladium on charcoal was very successful but - as might be expected[15] - over-reduction of the olefinic bonds always occurred. Of the methods that we tried the use of sodium and *t*-butanol in tetrahydrofuran at reflux was preferred by a wide margin. Tetrachlorobenzobarrelene (**4**) and its simple alkyl derivatives (**5**)-(**8**) are reductively dechlorinated in high yield (90-97%) under the preferred conditions[3] to the corresponding benzobarrelenes (**9**)-(**13**). Even the highly hindered 1,3,5-tri-*t*-butyltetrachlorobenzobarrelene (**8**) is reductively dechlorinated in almost quantitative yield. The compounds (**30**) and (**36**) were dechlorinated to afford the derivatives (**29**) and (**35**) in 85 and 87% yields respectively.

Preliminary results had indicated that a 1-alkoxy-group would survive the reduction and this observation[3] has been confirmed and extended: 1-methoxybenzobarrelene (**1**) and its alkyl derivatives (**14**)-(**20**) (93-98%) have been prepared by reductive dechlorination of the corresponding tetrachloro- derivatives (**21**)-(**28**). The analogous dibenzobarrelene (**29**) (85%) may be similarly prepared from (**30**). Although the 1-methoxy-group is highly allylic the C-O bond remains orthogonal to the π-bonds in the system and is preserved from reductive cleavage by stereoelectronic factors.[16] 1-Hydroxy-2,6-dimethylbenzobarrelene (**31**) is available by reductive dechlorination followed by a hydrolytic work-up of the corresponding trimethylsilylether (**32**) (72%). A less hindered alcohol might need protecting with a more adhesive silylether. Again, reductive cleavage of the trimethylsilyloxy group is not to be expected.



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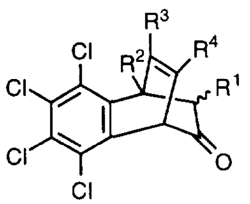

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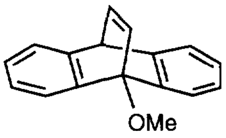

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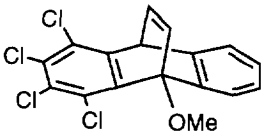

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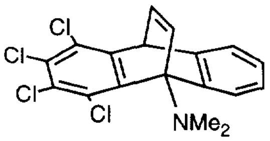

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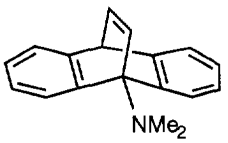

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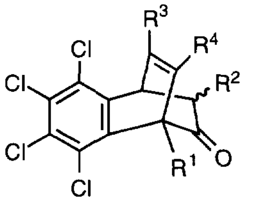

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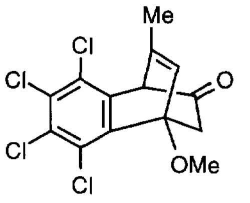

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Table 1

Benzobarrelene and benzobarrelenone derivatives prepared from pentachlorophenyllithium

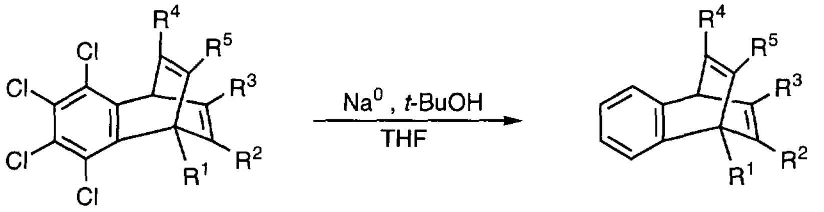
Compound Number	R^1	R^2	R^3	R^4	R^5	Yield (%)
(**5**)	Bu^t	H	H	H	H	9 (ref. 1c)
(**6**)	H	Bu^t	H	H	H	34 (ref. 1c)
(**7**)	Me	H	Me	Me	H	52 (ref. 1b)
(**8**)	Bu^t	H	Bu^t	Bu^t	H	69
(**25**)	OMe	H	Me	H	Me	46 [a]
(**37**)	H	Me	H	Me	-	16
(**27**)	OMe	Me	Me	H	Me	80 [b]
(**38**)	Me	Me	H	Me	-	12
(**28**)	OMe	Me	Me	Me	Me	90
(**30**)	-	-	-	-	-	70
(**32**)	$OSiMe_3$	Me	H	H	Me	34 [c]
(**36**)	-	-	-	-	-	77

[a] 4,6-Dimethyltetrachlorobenzobarrelenone (**37**) was also formed in a 16% yield.

[b] 3,4,6-Trimethyltetrachlorobenzobarrelenone (**38**) was also formed in a 12% yield.

[c] 1,3-Dimethyltetrachlorobenzobarrelen-2-one was also formed in a 34% yield.

Tertiary amines are also unaffected by the reduction conditions: 1-*N*,*N*-dimethylaminotetrachlorobenzobarrelene (**33**) is reduced to the *tetrakis*-deschloro analogue (**34**) (87%). Similarly, the related compound (**36**) is reductively dechlorinated and gave the compound (35) in 87% yield. The results relating to compounds with the general formulae indicated in Equation [**1**] are collected in Table 2 and show that alkyl-, alkoxy-, hydroxy- (as its trimethylsilylether) and dimethylamino-groups may be safely carried through the reductive dechlorination procedure.



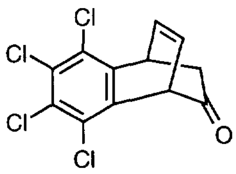
[**1**]

Table 2
The reductive dechlorination of tetrachlorobenzobarrelene derivatives

Compound Number	R^1	R^2	R^3	R^4	R^5	Yield (%)
(**1**)	MeO	H	H	H	H	98
(**9**)	H	H	H	H	H	90
(**10**)	*t*-Bu	H	H	H	H	93
(**11**)	H	*t*-Bu	H	H	H	94
(**12**)	Me	H	Me	Me	H	97
(**13**)	*t*-Bu	H	*t*-Bu	*t*-Bu	H	97
(**14**)	MeO	Me	H	H	H	93
(**15**)	MeO	Me	Me	H	H	93
(**16**)	MeO	Me	H	Me	H	95
(**17**)	MeO	H	Me	Me	H	98
(**18**)	MeO	Me	H	H	Me	96
(**19**)	MeO	Me	Me	Me	H	94
(**20**)	MeO	Me	Me	Me	Me	95
(**31**)	HO	Me	H	H	Me	72 [a]
(**34**)	Me_2N	H	H	H	H	87

[a] Obtained by the reductive dechlorination of compound (**32**).

The other common products of reactions between tetrachlorobenzyne and alkoxy- and dialkylamino-derivatives of benzene are derivatives of tetrachlorobenzobarrelenone (**39**).[1a,1f] Attempted reductive dechlorination of tetrachlorobenzobarrelenone (**39**) with sodium and *t*-butanol in boiling tetrahydrofuran gave mainly tetralin. It is likely that the ketone reduces and fragments to sodium ethenolate and a naphthalene derivative, which is then reduced to tetralin. Since both 1,2,3,4-tetrachloronaphthalene (**40**) and naphthalene are reduced to tetralin under these reaction conditions it is not possible to infer the point at which loss of the bridge occurs. Aromatisation of 2-hydroxy-2,3-dihydrobenzobarrelenes by loss of the hydroxyethano-bridge under basic conditions has been observed before;[17] we describe synthetic and analytical uses of related fragmentations in a separate paper.[18]



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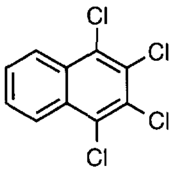

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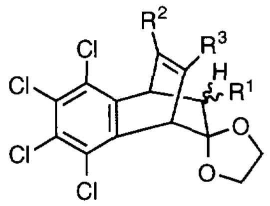
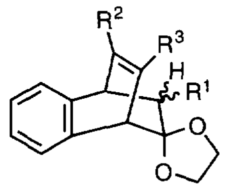
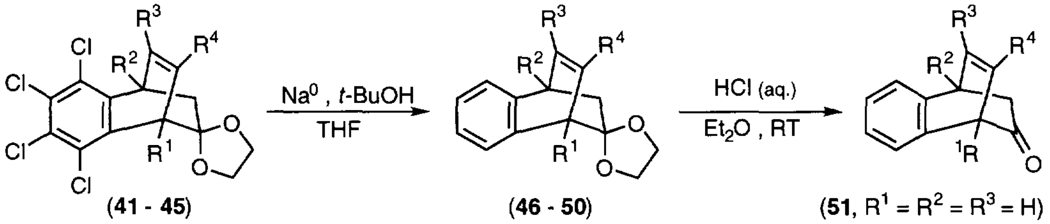


(**41**, $R^1 = R^2 = R^3 = H$)



(**46**, $R^1 = R^2 = R^3 = H$)

Tetrachlorobenzobarrelenones may be converted into their ethylene acetals in almost quantitative yield under mild conditions (ethylene glycol, boron trifluoride etherate, in dichloromethane) (*Table 3*).[4h,19] When such acetals (**41**)-(**45**) are subjected to reductive dechlorination with sodium-*t*-butanol (***Scheme 1***) they form benzobarrelenone acetals (**46**)-(**50**) in high yield (84-96%) (*Table 4*). The ethylene acetal may be easily cleaved (ethereal hydrochloric acid) to regenerate the carbonyl function. Thus, the acetal (**46**) was hydrolysed to benzobarrelenone (**51**) in a 98% yield. Under the conditions of the reduction neither ketones nor naphthalenes are stable; acetals are unaffected as are benzene rings and - in this case - double bonds.



Scheme 1

Table 3

The preparation of tetrachlorobenzobarrelenone ethylene acetal derivatives

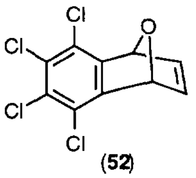
Compound number	R^1	R^2	R^3	R^4	Yield (%)
(**41**)	H	H	H	H	98
(**42**)	MeO	H	H	Me	95
(**43**)	H	MeO	H	H	88
(**44**)	H	MeO	Me	H	89
(**45**)	MeO	H	H	H	85

Table 4

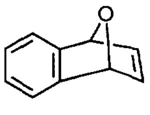
The reductive dechlorination of tetrachlorobenzobarrelenone ethylene acetal derivatives

Compound number	R^1	R^2	R^3	R^4	Yield (%)
(**46**)	H	H	H	H	85
(**47**)	MeO	H	H	Me	96
(**48**)	H	MeO	H	H	94
(**49**)	H	MeO	Me	H	98
(**50**)	MeO	H	H	H	96

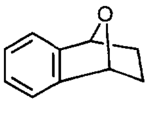
The third major class of tetrachlorobenzyne cycloadduct with arenes arises from reactions with furans and pyrroles.[2f,2g,11,20] Reductive dechlorination of 5,6,7,8-tetrachloro-1,4-dihydro-1,4-epoxynaphthalene (**52**)[11] gave a mixture of the desired product (**53**)[20] (40%) and 1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**54**)[20] (47%), the product of over-reduction. The mixture was separable by chromatography. The reduction of the olefinic bond was disappointing: the choice of sodium rather than lithium was intended to minimise over-reduction. Similarly the 1-methylpyrrole adduct (**55**)[2g] gave a chromatographically separable mixture of the desired product (**56**)[21] (38%) along with the product of over-reduction (**57**)[21,22] (50%); the 1,2,5-trimethylpyrrole adduct (**58**)[2f] gave analogous products (**59**) [35%][2f] and (**60**) [47%] respectively.



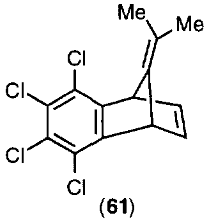
(**52**)



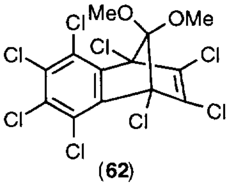
(**53**)



(**54**)



(**61**)



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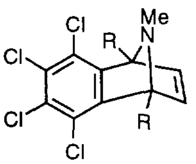
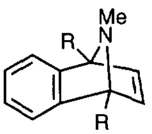
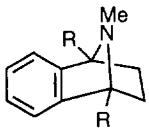


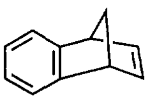
(**55**, R = H)
(**58**, R = Me)

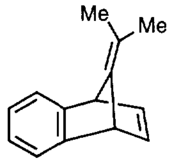


(**56**, R = H)
(**59**, R = Me)



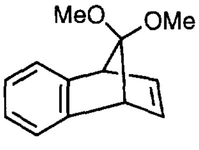
(**57**, R = H)
(**60**, R = Me)


(**63**)



(**64**)

The over-reduction could have been facilitated by strain in the double bond or by the proximity of a heteroatom. We prepared tetrachlorobenzonorbornadiene (**3**)[2h] and its 7-isopropylidene (**61**)[1d] and 7,7-dimethoxyperchloro (**62**) derivatives. Both tetrachlorobenzonorbornadiene (**3**) and its 7-isopropylidene derivative (**61**) were smoothly reduced by sodium-*t*-butanol to the expected products (**63**)[23] and (**64**)[24] in 83% and 93% yield respectively. However, 7,7-dimethoxyperchlorobenzonorbornadiene (**62**) did suffer some over-reduction: in addition to the expected product of dechlorination (**65**)[25] (66%) a small amount of 7,7-dimethoxybenzonorbornene (**66**)[25] (12%) was isolated.



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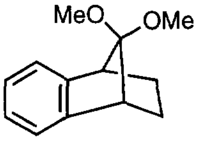

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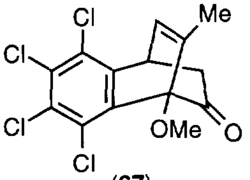

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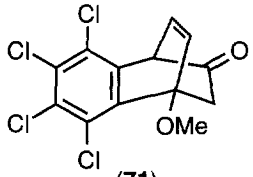

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It seems unlikely that strain alone can account for the over-reduction observed above. The presence of a coordinating heteroatom at or near the bridge seems to be required. Any factor that similarly lowers the π* orbital associated with the reducible bridge will favour over-reduction. The process is finely balanced and subtle changes will produce marked effects. The lack of over-reduction observed in the dechlorination of tetrachlorobenzobarrelenone acetals is notable in this context.

The scope of reductive dechlorination of tetrachlorobenzyne-arene cycloadducts with sodium-t-butanol-tetrahydrofuran may sometimes be limited by over-reduction. In the case of tetrachlorobenzobarrelenones suitable protecting groups prevent the problem. Some degree of over-reduction is observed with adducts of furans and pyrroles and with these heterocycles benzyne itself might be a suitable dienophile.[20] With the exception of such cases the use of tetrachlorobenzyne in tandem with reductive dechlorination of the adduct provides a practically useful route to benzobicyclic ring systems which are not easily available from benzyne and as such constitutes a very useful alternative to the use of benzyne itself.

The observation that the precipitate of sodium chloride formed during the reaction turns deep purple at the end of the reduction is intriguing. This prompted us to probe further into the detail of the reduction. The observation of coloured sodium chloride is not new. The colour is associated with the eponymous *F*-centres, which occur when electrons are incorporated into the sodium chloride lattice in place of chloride ions. An alternative representation is of sodium atoms incorporated into a chloride ion deficient salt lattice.[26]

Why should electrons build up in the sodium chloride lattice at the end of the reductive dechlorination. No doubt because they are no longer being removed. If this is so then during the reduction sodium atom doped sodium chloride acts as a reducing agent. Certainly, purple sodium chloride recovered from a reduction is itself capable of effecting reductive dechlorination : benzobarrelene **(9)** (7%) was obtained when tetrachlorobenzobarrelene **(4)** was subjected to the usual reduction using purple sodium chloride, freshly obtained from a similar reduction, in the place of sodium wire. Analysis of one sample of such purple sodium chloride showed it to contain approximately 27% of sodium as sodium (0). The purple sodium chloride reacts vigorously with water with effervescence and loss of colour. At the end of a normal reduction the excess of sodium separates as light bright globules: although it is difficult to exclude the possibility that small particles of sodium sand are sequestered in the denser purple sodium chloride it does seem that this electron-doped salt is a reducing agent in its own right.

What intermediates occur? There are no long-lived radicals that diffuse into the bulk solvent. A reduction conducted normally but in a mixture of tetrahydrofuran-tetrahydrofuran-d_8 (1:1) gave a product which had no detectable deuterium incorporation by mass spectrometry. There are no long-lived anions that diffuse into the bulk solvent. These reductions are conducted under conditions considerably more vigorous than those under which pentachlorophenyllithium decomposes to tetrachlorobenzyne.[11] The high yield and excellent mass balance are incompatible with any appreciable aryne formation in the bulk solvent. A reduction of 1-methoxy-2,3-dimethyltetrachlorobenzobarrelene **(23)** in *t*-butanol-*0-d* gave a product with very extensive deuterium incorporation. The amount of ^{1}H incorporated suggested a very large isotope effect for protonation : the % of [$^2H_4$]-**(15)** detected by mass spectrometry (35.26%) corresponds to an average probability for [^{2}H] incorporation at each step of 0.77. From this it follows that if the *t*-butanol-*0-d* were 98.5% [^{2}H], 1.5% [^{1}H] as claimed then the isotope effect for protonation averaged over each step and throughout the course of the reaction would be 19.6.

It is clear that the hydrogen involved in the hydrodechlorination arises from the hydroxylic proton of *t*-butanol, that if the anion diffuses into the bulk solvent then it is very rapidly protonated and that the intermediate aryl radical - if formed - does not diffuse into the bulk solution but is rapidly reduced to an aryl anion. In addition to providing the proton *t*-butanol plays another role. In a reduction conducted without *t*-butanol, in which we might have expected to divert the reaction from hydrodechlorination to other minor pathways not normally observed, tetrachlorobenzobarrelene **(4)** was recovered in 90% yield. The *t*-butanol clearly plays some role in initiating the reduction. The reduction appears to be initiated by the addition of 1,2-dichloroethane, or purple sodium chloride, or - significantly - by a catalytic amount of sodium chloride. These results may be interpreted within a mechanistic scheme in which reduction occurs by electron transfer to a molecule coordinated by a chlorine atom to a chloride site of a salt lattice on the surface of sodium metal. The resultant radical anion is equivalent to an aryl radical co-ordinated to salt. Cleavage of the C - Cl bond is facilitated by the fact that the chloride ion produced is formed in a very stable state. The aryl radical would be formed adjacent to a sodium ion; electron transfer through the salt lattice would occur faster than diffusion of the organic radical away from the lattice surface and would form an aryl sodium stabilised by complexation into a sodium chloride lattice. In this scheme the new Na(I) ions are initially formed remotely from the site of chloride ion deposition : these are ideal conditions for forming a lattice with a local deficiency in chloride ion, which would facilitate *F*-centre formation. It is easier to see why covalent chloride should coordinate to a salt lattice than to sodium metal. Tertiary butanol will react slowly at the surface of the sodium to form a layer of sodium *t*-butoxide. We believe that this, the necessary preliminary to the actual reduction, constitutes the initiation step. The activating effect of the easily reduced dichloroethane and of sodium chloride is easily understood in these terms.

The work described in this paper demonstrates the scope and utility of reductive dechlorination using sodium-t-butanol-tetrahydrofuran in the synthesis of polycyclic hydrocarbons. The good yields make this method very attractive and emphasise that tetrachlorobenzyne should be considered as an alternative reagent whenever benzyne itself appears to be required. The use of this reductive dechlorination in conjunction with our methods[18] for specifically removing one of the bridges from an arene-aryne cycloadduct constitutes a valuable method of benzannelation. We have prepared a large number of otherwise inaccessible compounds including those alkyl-substituted 1-methoxybenzobarrelenes that we required. The many and varied acid-catalysed rearrangements of these compounds will be reported separately. Elemental micro-analytical and other data are collected together in *Table 5*.

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Table 5

Analytical and other data

Cpd. No	Molecular formula	% Carbon (calc. value)	% Hydrogen (calc. value)	Melting point °C [a] (boiling point °C)	Mass spectrum m/z [b]
(**8**)	$C_{24}H_{30}Cl_4$	62.3 (62.6)	6.5 (6.5)	162-163	460 (M^+)
(**10**)	$C_{16}H_{18}$			60-61	210 (M^+)
(**11**)	$C_{16}H_{18}$	91.7 (91.4)	8.5 (8.6)	(105-106 at 0.2 mm)	210 (M^+)
(**12**)	$C_{15}H_{16}$	92.0 (92.0)	7.9 (8.0)	85-88	196 (M^+)
(**13**)	$C_{24}H_{34}$	89.4 (89.4)	10.2 (10.5)	139-140	322 (M^+)
(**14**)	$C_{14}H_{14}O$	84.7 (84.8)	7.0 (7.1)	(122-123 at 4.5 mm)	198 (M^+)
(**15**)	$C_{15}H_{16}O$	84.6 (84.9)	7.7 (7.6)	80-81	212 (M^+)
(**16**)	$C_{15}H_{16}O$	84.5 (84.9)	7.5 (7.6)	(118-120 at 0.3 mm)	212 (M^+)
(**17**)	$C_{15}H_{16}O$	84.8 (84.9)	7.5 (7.6)	69-70	212 (M^+)
(**18**)	$C_{15}H_{16}O$	84.9 (84.9)	7.6 (7.6)	74-76	212 (M^+)
(**19**)	$C_{16}H_{18}O$	84.4 (85.0)	8.1 (7.8)	56-57	226 (M^+)
(**20**)	$C_{17}H_{20}O$	85.1 (85.0)	8.3 (8.3)	111-112	240 (M^+)
(**25**)	$C_{15}H_{12}Cl_4O$	51.3 (51.5)	3.4 (3.4)	125-126	350 (M^+)
(**27**)	$C_{16}H_{14}Cl_4O$	52.4 (52.5)	4.3 (4.4)	139-140	–
(**28**)	$C_{17}H_{16}Cl_4O$	53.5 (53.4)	4.2 (4.3)	166-167	378 (M^+)
(**29**)	$C_{17}H_{14}O$	87.1 (87.2)	6.1 (6.0)	181-182	234 (M^+)
(**30**)	$C_{17}H_{10}Cl_4O$	54.7 (54.9)	2.8 (2.7)	191-193	372 (M^+)
(**31**)	$C_{14}H_{14}O$	84.6 (84.8)	7.1 (7.1)	95-96	198 (M^+)
(**32**)	$C_{17}H_{18}Cl_4OSi$	49.6 (50.0)	4.3 (4.4)	132-133	408 (M^+)
(**34**)	$C_{14}H_{15}N$	–	–	68-69	197 (M^+)
(**35**)	$C_{18}H_{17}N$	87.4 (87.4)	6.9 (6.9) [c]	184-185	247 (M^+)
(**36**)	$C_{18}H_{13}Cl_4N$	56.1 (56.1)	3.4 (3.4) [d]	196-197	385 (M^+)
(**37**)	$C_{14}H_{10}Cl_4O$	49.8 (50.0)	3.0 (3.0)	170-171	294 (M^+ - 42)
(**38**)	$C_{15}H_{12}Cl_4O$	51.3 (51.4)	3.4 (3.4)	145-146	294 (M^+ - 56)
(**41**)	$C_{14}H_{10}Cl_4O_2$	47.6 (47.7)	2.7 (2.8)	111-112	–
(**42**)	$C_{16}H_{14}Cl_4O_3$	48.2 (48.5)	3.4 (3.6)	116-117	310 (M^+ - 86)
(**43**)	$C_{15}H_{12}Cl_4O_3$	47.1 (47.1)	3.1 (3.2)	129-130	296 (M^+ - 86)
(**44**)	$C_{16}H_{14}Cl_4O_3$	48.6 (48.5)	3.6 (3.6)	155-156	310 (M^+ - 86)
(**45**)	$C_{15}H_{12}Cl_4O_3$	–	–	185-186	296 (M^+ - 86)
(**46**)	$C_{14}H_{14}O_2$	78.9 (78.5)	6.7 (6.6)	115-117	214 (M^+)
(**47**)	$C_{16}H_{18}O_3$	74.2 (74.4)	6.9 (7.0)	85-86	172 (M^+ - 86)
(**48**)	$C_{15}H_{16}O_3$	73.4 (73.8)	6.0 (6.6)	124-125	158 (M^+ - 86)
(**49**)	$C_{16}H_{18}O_3$	74.3 (74.4)	6.9 (7.0)	118-120	172 (M^+ - 86)
(**50**)	$C_{15}H_{16}O_3$	74.3 (73.8)	6.6 (6.6)	120-121	158 (M^+ - 86)
(**67**)	$C_{14}H_{10}Cl_4O_2$	47.6 (47.7)	2.9 (2.8)	164-165	310 (M^+ - 42)
(**68**)	$C_{14}H_{10}Cl_4O_2$	48.1 (47.7)	2.9 (2.8)	155-156	296 (M^+ - 56)
(**70**)	$C_{14}H_{10}Cl_4O_2$	47.3 (47.7)	2.8 (2.8)	160-162	310 (M^+ - 42)

[a] All solids recrystallised from ethanol except (**41**) from hexane and (**46**) from light petroleum, b.p. 40-60 °C.

[b] M/z is for the [$^{35}Cl_4$] containing ion, the most abundant in the [Cl_4] cluster.

[c] N 5.5 (5.7%).

[d] N 3.5 (3.7%).

Experimental

General Procedures.- All reductive dechlorinations and reactions involving organometallic reagents were carried out in oven-dried glassware under an atmosphere of dry, oxygen-free nitrogen. All solvents were distilled and dried to the appropriate degree by conventional methods before use; the tetrahydrofuran used in reductive dechlorinations was stored over sodium wire. Light petroleum refers to the fraction boiling between 60-80°C unless otherwise stated. Analytical t.l.c. was carried out using 0.25mm thick layers of silica-gel (GF254); preparative t.l.c. was carried out using 1.0 mm thick layers of silica-gel (PF254). Analytical g.l.c. was carried out using a Pye 104 series gas chromatograph fitted with a flame ionisation detector. Infra-red spectra were determined for potassium bromide discs, thin films, or solutions in chloroform, on a Perkin-Elmer 257 spectrophotometer. Ultraviolet spectra were determined on a Pye SP 8000 spectrophotometer. ^{1}H-n.m.r. spectra were determined for approximately 20% w/v solutions containing tetramethylsilane as internal standard at 90 MHz on a Perkin-Elmer R32 spectrometer. Mass spectra were determined on an A.E.I. MS12 mass spectrometer. Melting points were determined on a Koffler hot-stage apparatus, and are uncorrected.

Method A.- Addition of tetrachlorobenzyne to arenes.

(a) 1,3,9-Tri-*t*-butyl-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene (1,3,5-tri-*t*-butyltetrachlorobenzobarrelene) (8).

A stirred solution of pentachlorophenyllithium [from hexachlorobenzene (50 mmol) and *n*-butyllithium (69 mmol; as a solution in hexane) prepared and maintained at - 78°C in ether (*ca.*200 mL)] was treated with 1,3,5-tri-*t*-butylbenzene (42.0 g, 152 mmol). The reaction mixture was allowed to warm to 24-25°C and stirred at this temperature for 58h. The reaction mixture was diluted with ether (100 mL), washed with dilute hydrochloric acid (2*N*; 100 mL) and water (2x100 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the involatile residue was purified by chromatography on alumina. Elution with 9:1 light-petroleum:ether gave 1,3,9-tri-*t*-butyl-5,6,7,8-tetrachloro-1,4-dihydro-1,4- ethenonaphthalene (1,3,5-tri-*t*-butyltetrachlorobenzobarrelene) **(8)** (15.8 g, 69%), m.p. 162-163°C (from ethanol) (Found: C, 62.3; H, 6.5. $C_{24}H_30Cl_4$ requires C, 62.6; H, 6.5%); ν_{max} (KBr) 3 100, 3 040, 2 985, 2 975, 2 915, 2 875, 1 480 1 462, 1 403, 1 390, 1 380, 1 365, 1 335, 1 235, 1 170, 1 120, 1 090, 940, 845, 828, 765, 710, and 668 cm^{-1} δ_H (90 MHz; $CDCl_3$) 1.07 (18H, s), 1.21 (3H, s), 1.69 (6H, s), 5.34 (1H, t, *J* 2Hz), and 6.29 (2H, d, *J* 2Hz); *m/z* 460 (M^+).

(b) 5,6,7,8-Tetrachloro-1,4-dihydro-2,10-dimethyl-1-trimethylsilyloxy-1,4-ethenonaphthalene (2,6-dimethyl-1-trimethylsilyloxytetrachlorobenzobarrelene) (32).

In a similar reaction to **A (a)** a solution of pentachlorophenyllithium (*ca.* 50 mmol) in ether was treated at -78°C with 2,6-dimethylphenyl trimethylsilyl ether (42.0 g, 216 mmol). The crude product obtained by the method of **A(a)** was purified by chromatography on silica-gel. Elution with 9:1 light-petroleum:ether gave 5,6,7,8-tetrachloro-1,4-dihydro-2,10-dimethyl-1-trimethylsilyloxy-1,4-ethenonaphthalene (2,6-dimethyl-1- trimethylsilyloxytetrachlorobenzobarrelene) **(32)** (6.5 g, 34%), m.p. 132-133°C (from ethanol) (Found: C, 49.6; H, 4.3. $C_{17}H_{18}Cl_4SiO$ requires C, 50.0; H, 4.4%); ν_{max} (KBr) 3 065, 3 015, 2 965, 2 925, 2 850, 1 448, 1 430, 1 365, 1 345, 1 290, 1 265, 1 250, 1 190, 1 113, 1 018, 968, 938, 921, 885, 840, 825, 790, 755, and 710 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.42 (9H, s), 1.92 (6H, d, *J* 2Hz), 5.02 (1H, t, *J* 7Hz), and 6.28-6.55 (2H, m); *m/z* 408 (M^+). Further elution gave 5,6,7,8-tetrachloro-3,4-dihydro-1,3-dimethyl-1,4-ethenonaphthalen-2(1*H*)-one (1,3-dimethyl-tetrachlorobenzobarrelenone) (5.6 g, 34%), m.p. 139-140°C (from ethanol) (lit.,[1f] 139-140°C).

Method B.- Conversion of benzobarrelenones into their ethylene acetals. 5',6',7',8'-Tetrachloro-3',4'-dihydrospiro[1,3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrotetrachlorobenzobarrelene) (41)

A solution of 5,6,7,8-tetrachloro-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (tetrachlorobenzobarrelenone) **(39)** (0.470 g, 1.52 mmol) in a mixture of boron trifluoride etherate (10 mL), 1,2-dihydroxyethane (10 mL), and dichloromethane (50 mL) was kept at room temperature for 50h. The reaction mixture was washed with water (25 mL), saturated aqueous sodium bicarbonate (2 x 25 mL), and water (25 mL), and then evaporated under reduced pressure to give an orange oil that was purified by chromatography on silica-gel. Elution with 4:1 light-petroleum (b.p. 60-80°C):ether gave 5',6',7',8'-tetrachloro-3',4'-dihydrospiro[1,3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrotetrachlorobenzobarrelene) **(41)** (0.520 g, 98%), m.p.111-112°C (from hexane) (Found: C, 47.6; H, 2.7. $C_{14}H_{10}Cl_4O_2$ requires C, 47.7; H, 2.8%), ν_{max} ($CHCl_3$) 2 895, 1 380, 1 350, 1 335, 1 280, 1 245, 1 225, 1 160, 1 140, 1 125, 1 065, 1 030, 990, 950, 680, and 650 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.80 (1H, dd, *J* 3 and 14 Hz), 2.0 (1H, dd, *J* 3 and 14 Hz), 3.70-4.30 (4H, m), 4.40-4.60 (2H, m), and 6.48-6.70 (2H, m).

Method C. - Reductive dechlorination.

(a) 1,4-Dihydro-1-methoxy-1,4-etheno-naphthalene (1-methoxybenzobarrelene) (1)

Sodium wire (20 g) in tetrahydrofuran (600 mL) that was being heated under reflux was treated sequentially with *t*-butanol (60 mL) and a solution of 5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene **(21)** (20.4 g, 63.4mmol) in tetrahydrofuran (200 mL). The reaction mixture was heated under gentle reflux until the precipitate of sodium chloride became deep purple. The reaction mixture was allowed to cool to room temperature and then filtered through glass-wool into methanol (50 mL). After any small pieces of sodium had reacted with the methanol the filtrate was diluted with water (500 mL) and extracted with ether (6 x 200 mL). The combined ethereal phases were washed with saturated aqueous sodium chloride (2 x 250 mL), dried ($MgSO_4$), and carefully evaporated under reduced pressure. The residual oil was absorbed onto sufficient alumina to produce a free-running powder that was loaded onto an alumina chromatography column. Elution with light-petroleum gave a pale yellow oily solid (98%) that was recrystallised from light-petroleum to give 1,4-dihydro-1-methoxy-1,4-ethenonaphthalene (1-methoxybenzobarrelene) **(1)** (10.5g, 90%), m.p. 36-37°C (from light-petroleum) (lit.,[4f] 37-38°C).

(b) 3',4'-Dihydrospiro[1,3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrobenzobarrelene) (46)

In a similar reaction to **C(a)** carried out on a proportionately smaller scale 5',6',7',8'-tetrachloro-3',4'-dihydrospiro[1,3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrotetrachlorobenzobarrelene) **(41)** (0.770 g, 2.2 mmol) gave a crude product that was purified by preparative t.l.c. on silica-gel using 4:1 light-petroleum:ether as eluant to give 3',4'-dihydrospiro[1,3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrobenzobarrelene) **(46)** (0.400 g, 85%), m.p. 115-117°C (from light petroleum) (Found: C, 78.9; H, 6.7. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%); ν_{max} (KBr) 2 960, 2 855, 1 468, 1 455, 1 434, 1 340, 1 310, 1 265, 1 250, 1 215, 1 115, 1 095, 1 045, 1 010, 965, 950, 910, 860, 825, 785, 760, 710, and 670 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.8 (1H, dd, *J* 3 and 14 Hz), 2.0 (1H, dd, *J* 3 and 14 Hz), 3.75-4.1 (6H, m), 6.45-6.8 (2H,m), and 7.0-7.3 (4H, m); *m/z* 214(M$^+$).

(c) 1,4-Dihydro- and 1,2,3,4-tetrahydro-1,4,9-trimethyl-1,4-iminonaphthalenes (59) and (60)

A solution of 5,6,7,8-tetrachloro-1,4-dihydro-1,4,9-trimethyl-1,4-iminonaphthalene (58) (6.0 g, 18.58 mmol) in tetrahydrofuran (50 mL) was added to and allowed to react with a mixture of sodium wire (6.6 g, 276 mg-atom), *t*-butanol (20 g), and tetrahydrofuran (300 mL) as described in **C(a)**. The crude product obtained by this method was purified by chromatography on silica-gel to give (i) 1,4-dihydro-1,4,9-trimethyl-1,4-iminonaphthalene (**59**) (1.25 g, 35%), 45-46°C, and (ii) 1,2,3,4-tetrahydro-1,4,9-trimethyl-1,4-iminonaphthalene (**60**) (1.64 g, 47%), m.p. 41-42°C. The spectroscopic data for these products were concordant with published data.

Method D. - 1,4-Dihydro-1-hydroxy-2,10-dimethyl-1,4-ethenonaphthalene (1-hydroxy-2,6-dimethylbenzobarrelene) (31).

A solution of 5,6,7,8-tetrachloro-1,4-dihydro-2,10-dimethyl-1-trimethylsilyloxy-1,4-ethenonaphthalene (2,6-dimethyl-1-trimethylsilyloxy-tetrachlorobenzobarrelene) **(32)** (2.50 g, 6.13 mmol) in tetrahydrofuran (25 mL) was added to and allowed to react with a mixture of sodium wire (3.0 g, 123 mg-atoms), *t*-butanol (9.0 g), and tetrahydrofuran (400 mL) by method **C(a)**. The crude product was purified by chromatography on alumina. Elution with light-petroleum gave 1,4-dihydro-1-hydroxy-2,10-dimethyl-1,4-etheno-naphthalene (1-hydroxy-2,6-dimethylbenzobarrelene) **(31)** (0.900 g, 72%), m.p. 95-96°C (from ethanol). (Found: C, 84.6; H, 7.1. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); ν_{max} (KBr) 3 450, 3 060, 3 040, 2 920, 2 850, 1 600, 1 475, 1 445, 1 405, 1 382, 1 348, 1 320, 1 310, 1 220, 1 180, 1 080, 1 025, 945, 890, 875, 840, 765, 760, 742, and 700cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.88 (1H, br.s), 2.30 (6H, s), 3.51 (1H, m), 7.08-7.68 (6H, m); *m/z* 198 (M$^+$).

Method E. - 3,4-Dihydro-1,4-ethenonaphthalen-2(1*H*)-one (benzobarrelenone) (51) by acetal hydrolysis

A stirred solution of 3',4'-dihydrospiro[1.3]-dioxolane-2,2'(1'*H*)-[1,4]ethenonaphthalene (2,2-ethylenedioxy-2,3-dihydrobenzobarrelene) **(46)** (0.510 g, 2.43 mmol) in ether (25 mL) and concentrated hydrochloric acid (3 drops) was maintained at room temperature for 0.5h. The reaction mixture was diluted with water (20 mL) and extracted with ether (2 x 25mL). The ethereal phases were combined, washed with saturated aqueous sodium bicarbonate (20 mL) and water (20 mL) and then dried ($MgSO_4$). The extract was evaporated carefully under reduced pressure and the residue was purified by preparative t.l.c. Elution with 4:1 light-petroleum:ether gave 3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (benzobarrelenone) **(51)** (0.406 g, 98%) as an oily solid (lit.[27] m.p. 56-58°C). δ_H (60 MHz; $CDCl_3$) 1.7-2.5 (2H, ddd, *J*18 and 3 and 3 Hz), 3.1-3.4 (1H, m), 4.43 (1H, dd, *J*6 and 3 Hz), 6.4-6.95 (2H, m), and 7.05-7.45 (4H, m), concordant with spectra previously reported.

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