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Rearrangement Reactions of Bicyclic Systems: Part VI.[1] A [^{14}C]-Tracer Study of the Acid-Catalysed Skeletal Rearrangement of 1,4-Dihydro-1-methoxy-1,4-etheno-naphthalene (1-Methoxybenzobarrelene) and its 5,6,7,8-Tetrahalogeno-derivatives

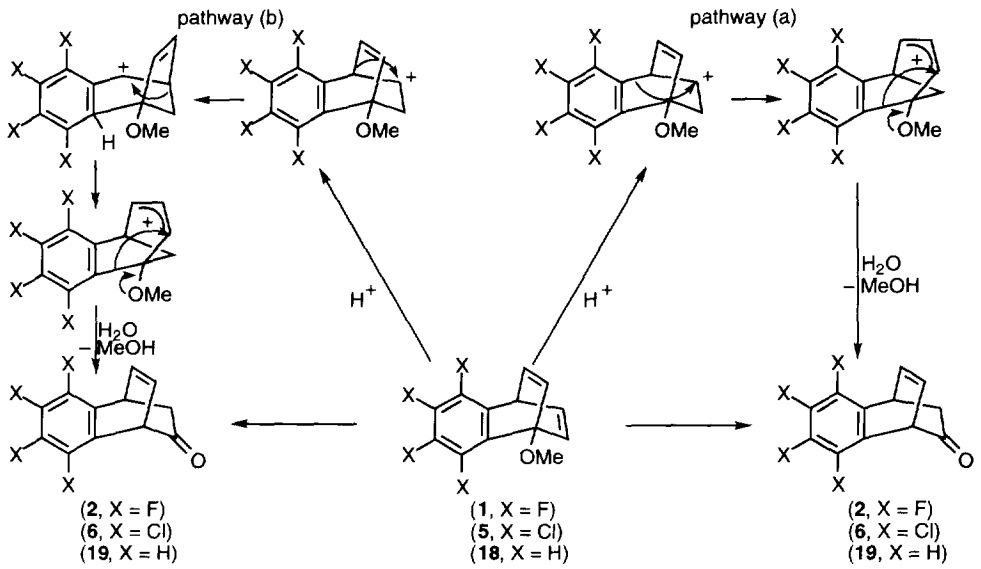
Neil J. Hales, Harry Heaney,* and John H. Hollinshead

Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

Abstract: *A degenerate skeletal rearrangement occurs during the acid catalysed conversion of 1-methoxybenzobarrelene and its tetrachloro- and tetrafluoro-derivatives into the corresponding 3,4-dihydro-1,4-ethenonaphthalen-2(1H)-ones (benzobarrelenones). A [^{14}C]-tracer study has confirmed that two pathways operate. In both pathways the methoxylated bridgehead C-1 of the benzobarrelene becomes the carbonyl C-2 of the benzobarrelenone. The pathways are distinguished by the fate of the benzobarrelene bridgehead C-4: in one pathway aryl migration leaves this formerly bridgehead C-4 as the olefinic C-5 of the newly formed benzobarrelenone; in the other pathway the bridgehead C-4 remains bonded to the aryl ring while a double migration of other skeletal bonds leaves it as the bridgehead C-4 of the benzobarrelenone. The pathway involving aryl migration is favoured in each case examined. The preference for aryl migration is greater in concentrated (> 98%) sulphuric acid than in aqueous (80%) sulphuric acid and in both cases the preference increases as the aryl substitution varies from F_4 to Cl_4 to H_4.*

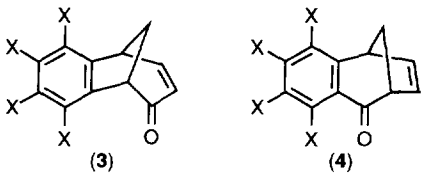
Introduction

The complex and subtle rearrangements of benzobarrelenes and their analogues have held a fascination for organic chemists for many years.[2,3] Our published work in this area[3] has indicated that it may not always even be apparent to what extent rearrangement has occurred. For instance, in the rearrangement of 1-methoxytetrafluorobenzobarrelene (**1**) into tetrafluorobenzobarrelenone (**2**)[3d,4b] there is no *prima facia* case for invoking a skeletal rearrangement at all: a sequence of functional group transformations involving such intermediates as a bridgehead carbenium ion or an *O*-methyloxiranium ion can account for the apparent course of the reaction and such a sequence - albeit a stereochemically disfavoured one - has been proposed.[4] However, in similar rearrangements of species bearing methyl group- or [^{2}H]-labels we have already shown[3d-g] that the overall rearrangement of the substituent locants is so extensive that the reaction is probably best explained by the proximal protonation followed by at least two competing degenerate skeletal rearrangements (Scheme 1) and that the balance between these pathways is sensitive to the reaction conditions. The observation[4b] that rearrangement of 1-methoxytetrafluorobenzobarrelene (**1**) in [$^2H_2$]sulphuric acid gives 3-[^{2}H]tetrafluorobenzo--barrelenone (3-[^{2}H]-**2**) is also consistent with this mechanism. Unfortunately methyl-labels perturb the course of the reaction[2g,2i,3e-g] and [^{2}H]-labels may be lost or rearrange independently of the carbon skeleton under acid-catalysed conditions. We decided to investigate the degenerate skeletal rearrangement using [^{14}C]-labelling.



Scheme 1

Minor pathways that lead by distal protonation to trace amounts of benzobicyclo[3.2.1]octadienones such as (**3**) and (**4**) were not considered here.[3]



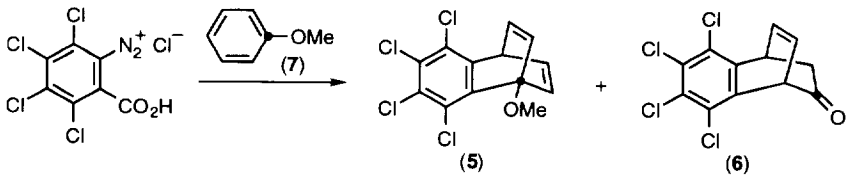
We have already described the necessary preparatory work: how 1-methoxybenzobarrelenes and benzobarrelenones can be degraded and how selected atoms from the bicyclic ring can be isolated;[5] how 1-methoxybenzobarrelenes can be prepared by dehalogenation of their tetrachloro-derivatives;[6] how 1-methoxy-tetrahalogenobenzobarrelenes can be prepared from tetrahalogenobenzynes and anisoles;[7] and how anisoles may be synthesised in specifically 1- and 4-[^{14}C]-labelled form.[8] We have carried out acid-catalysed skeletal rearrangements of simple radiolabelled 1-methoxybenzobarrelenes and we now report details of the effect of varying both acid strength and aromatic substitution on the two competing pathways and on the balance between them.

Results and Discussion

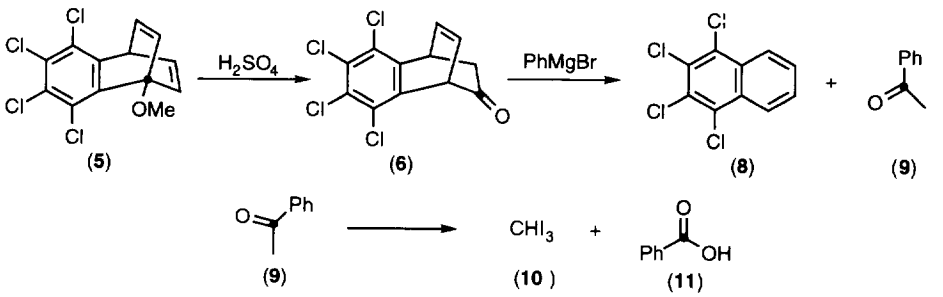
Rearrangements at C1: a common pathway

1-[^{14}C]-1-Methoxytetrachlorobenzobarrelene (1-[^{14}C]-**5**) (major product) and 2-[^{14}C]-tetrachlorobenzobarrelenone (1-[^{14}C]-**6**) (minor product) were prepared[7] by reaction of tetrachlorobenzyne with 1-[^{14}C]-anisole (1-[^{14}C]-**7**)[8] (Scheme 2). The position of the label in these products followed unambiguously from their

method of synthesis - 1,4-cycloaddition[9] to specifically *C*-1 labelled anisole - and is also confirmed by the results of this study. The isolation of the minor product, the 2-[^{14}C]-labelled benzobarrelenone (2-[^{14}C]-**6**), is useful here because it provides a reference sample with which the distribution of radiolabel in the *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**) produced by rearrangement can be compared.



Scheme 2



Scheme 3

Table 1.
Radioactivity of 1-[^{14}C]-1-methoxytetrachlorobenzobarrelene (1-[^{14}C]-**5**) and of the products of its rearrangement and degradation

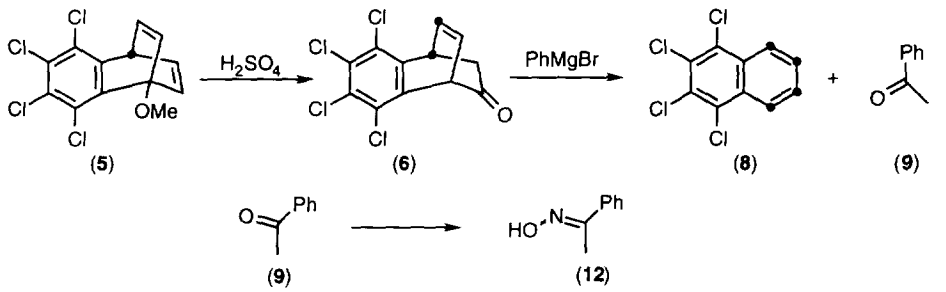
Compound No.	Compound Name	Activity / μc/mole (standard deviation)
(**10**)	Iodoform [a]	0.575 (0.615)
(**8**)	1,2,3,4-tetrachloronaphthalene [a]	0.405 (0.482)
([^{14}C]-**11**)	Benzoic acid [a]	210.9 (1.023)
(**10**)	Iodoform [b]	c
(**8**)	1,2,3,4-tetrachloronaphthalene [b]	0.472 (0.442)
([^{14}C]-**11**)	Benzoic acid [b]	213.6 (1.30)

[a] From x-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**)
[b] From 2-[^{14}C]tetrachlorobenzobarrelenone (2-[^{14}C]-**6**)
[c] Not obtained pure
1 μc = 2.22E6 dpm

1-[^{14}C]-1-Methoxytetrachlorobenzobarrelene (1-[^{14}C]-**5**) was converted into *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**) by acid-catalysed rearrangement in concentrated sulphuric acid[3d] (Scheme 3). Phenylmagnesium bromide induced fragmentation[5] of both of the [^{14}C]-labelled tetrachlorobenzobarrelenones (2-[^{14}C]-**6**) and (x-[^{14}C]-**6**) into 1,2,3,4-tetrachloronaphthalene (**8**) and *x*-[^{14}C]-acetophenone (x-[^{14}C]-**9**) and thence into iodoform (**10**) and *x*-[^{14}C]-benzoic acid (x-[^{14}C]-**11**) gave only one significantly radioactive fragment: benzoic acid (Table 1). Since this was derived entirely from *C*-1 of 1-[^{14}C]-anisole (1-[^{14}C]-**7**) and *C*-2 of the [^{14}C]-labelled tetrachlorobenzobarrelenones (2-[^{14}C]-**6**) and (x-[^{14}C]-**6**), the acid-catalysed rearrangement 1-methoxytetrachlorobenzobarrelene (**5**) in concentrated sulphuric acid at room temperature gives tetrachlorobenzobarrelenone (**6**) by pathways that all involve migration of *C*-1 to *C*-2 (Scheme 1)

Rearrangements at C4: diverse pathways

4-[^{14}C]-1-Methoxytetrachloro-benzobarrelene (4-[^{14}C]-**5**) was prepared from 4-[^{14}C]-anisole (4-[^{14}C]-**7**) by methods similar to those described in the previous section (Scheme 2) and converted into *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**) by acid-catalysed rearrangement in concentrated sulphuric acid at room temperature (Scheme 4). The *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**) was degraded (Scheme 4) by phenylmagnesium bromide induced fragmentation to give acetophenone (**9**), which was characterised as its oxime (**12**)[10] and was not significantly radioactive, and *x*-[^{14}C]-tetrachloronaphthalene (x-[^{14}C]-**8**), which contained all of the radioactivity (Table 2).



Scheme 4

A second sample of *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**) was reductively dechlorinated[6] as its ethylene acetal (x-[^{14}C]-**13**). The *x*-[^{14}C]-benzobarrelenone (x-[^{14}C]-**6**) so obtained was degraded to *x*-[^{14}C]-naphthalene (x-[^{14}C]-**8**) (Scheme 5), which was then converted[6] by reaction with tetrachlorobenzyne into *x*-[^{14}C]-tetrachlorodibenzobarrelene (x-[^{14}C]-**14**). The labelled acetal (x-[^{14}C]-**13**) had been dechlorinated[6] because it is not practicable to react 1,2,3,4-tetrachloronaphthalene (**8**) with tetrachlorobenzyne. The labelled tetrachlorobenzyne adduct (x-[^{14}C]-**14**) was then fragmented to afford *x*-[^{14}C]-1,2,3,4-tetrachloroanthracene (x-[^{14}C]-**15**) and *x*-[^{14}C]-3,6-di-(2'-pyridyl)pyridazine (x-[^{14}C]-**16**) by reaction with di-2'-pyridyl-*s*-tetrazine (**17**) (Scheme 6) (Table 2).

Table 2.

Radioactivity of the 4-[^{14}C]-1-methoxybenzobarrelenes 4-[^{14}C]-**1**, 4-[^{14}C]-**5**, and 4-[^{14}C]-**18** and of the products of their rearrangement and degradation

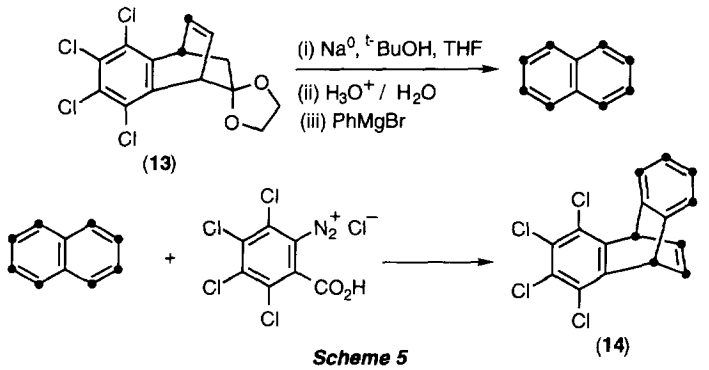
Compound Number	Compound Name	Activity / μc /mole x 10^2			
		Conc. sulfuric acid		80% sulfuric acid	
		Run 1	Run 2	Run 3	Run 4
From 1-Methoxytetrachlorobenzobarrelene 4-[^{14}C]-**5**					
4-[^{14}C]-**5**	1-Methoxytetrachlorobenzobarrelene 4-[^{14}C]-**5**	7.2	4.07	7.2	4.07
x-[^{14}C]-**6**	Tetrachlorobenzobarrelenone	7.31	4.06	7.31	4.06
x-[^{14}C]-**8**	Tetrachloronaphthalene	7.34	–	7.22	–
12	Acetophenone oxime	–[a]	–	–[a]	–
x-[^{14}C]-**15**	Tetrachloroanthracene	–	2.21	–	2.35
x-[^{14}C]-**16**	3,6-Di-(2'-pyridyl)pyridazine	–	[1.85][b]	–	1.71][b]
From 1-Methoxybenzobarrelene 4-[^{14}C]-**18**					
4-[^{14}C]-**18**	1-Methoxybenzobarrelene	4.14	–	4.14	–
x-[^{14}C]-**19**	Benzobarrelenone	4.21	–	4.21	–
12	Acetophenone oxime	–[a]	–	–[a]	–
x-[^{14}C]-**15**	Tetrachloroanthracene	2.17	–	[4.01][b,d]	–
x-[^{14}C]-**16**	3,6-Di-(2'-pyridyl)pyridazine	1.96	–	0.20[d]	–
From 1-Methoxytetrafluorobenzobarrelene 4-[^{14}C]-**1**					
4-[^{14}C]-**1**	1-Methoxytetrafluorobenzobarrelene	4.34	–	4.34	–
x-[^{14}C]-**2**	Tetrafluorobenzobarrelenone	4.37	–	4.37	–
x-[^{14}C]-**20**	Tetrafluoronaphthalene[c]	[2.70][b]	–	[2.88][b]	–
x-[^{14}C]-**16**	3,6-Di-(2'-pyridyl)pyridazine	1.67	–	1.49	–

[a] Indistinguishable from background level of radioactivity

[b] By difference: insufficient purified sample available for accurate counting

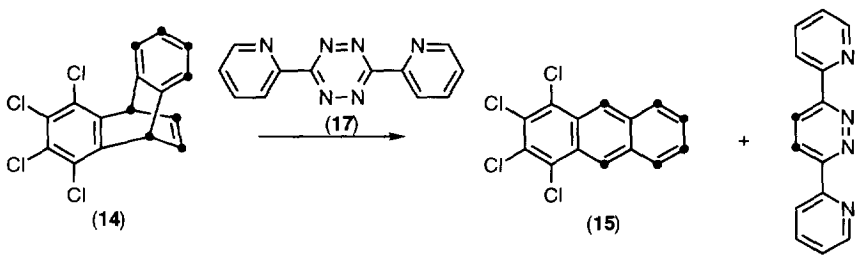
[c] From tetrafluorobenzobarrelene x-[^{14}C]-**22**

[d] The 3,6-di-(2'-pyridyl)pyridazine x-[^{14}C]-**16** of this set could not be purified and these results are regarded as unreliable



Scheme 5

The results are consistent with the operation of at least two rearrangement routes:[3d] the major route (a) involving aryl rearrangement from *C*-4 to *C*-5 and the minor route (b) involving etheno-bridge migration from *C*-4 to *C*-5. Subsequent rearrangements of the initially formed mixture of cations produce tetrachlorobenzobarrelenone by two different routes (Scheme 1), in which the major aryl-migratory route (a) predominates by a factor of about 10 under these conditions (Table 2).



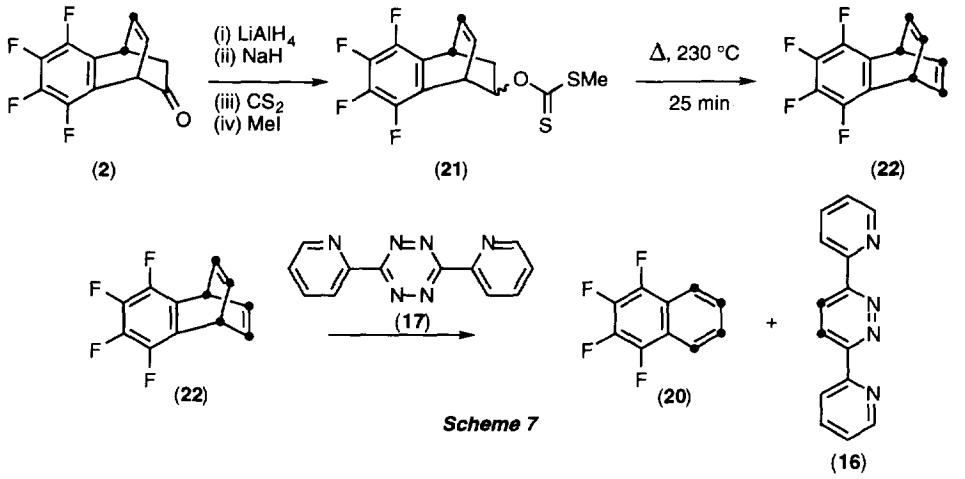
Scheme 6

Rearrangements at *C*-4: Effect of aryl substitution

4-[^{14}C]-1-Methoxytetrafluorobenzobarrelene (4-[^{14}C]-**1**) was prepared[7] by the addition of tetrafluorobenzyne to 4-[^{14}C]-anisole (4-[^{14}C]-**7**)[8] and 4-[^{14}C]-1-methoxybenzobarrelene (4-[^{14}C]-**18**) was prepared by reductive dechlorination[6,11a,11b] of 4-[^{14}C]-1-methoxytetrachlorobenzobarrelene (4-[^{14}C]-**5**). Acid-catalysed rearrangement of these labelled benzobarrelenes (4-[^{14}C]-**18**) and (4-[^{14}C]-**1**) gave *x*-[^{14}C]-tetrafluorobenzobarrelenone (x-[^{14}C]-**2**) and *x*-[^{14}C]-benzobarrelenone (x-[^{14}C]-**19**) respectively (Scheme 1, X = F and X = H).

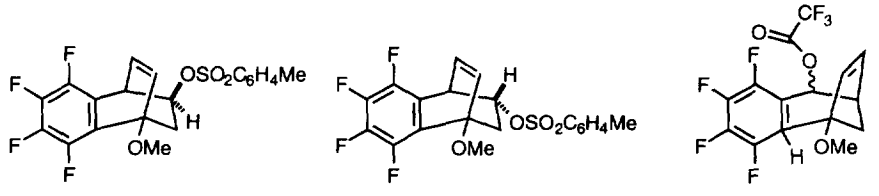
The degradation of *x*-[^{14}C]-tetrafluorobenzobarrelenone (x-[^{14}C]-**2**) is problematical. We could not directly apply the methods described above since arynes do not react well with 1,2,3,4-tetrafluoronaphthalene (**20**) and no effective reductive defluorination exists. *x*-[^{14}C]-Tetrafluorobenzobarrelenone (x-[^{14}C]-**2**) was converted *via* reduction and pyrolysis of the corresponding xanthate esters (x-[^{14}C]-**21**) into *x*-[^{14}C]-tetrafluorobenzobarrelene (x-[^{14}C]-**22**),[5] which was then fragmented (Scheme 7) by treatment with 3,6-di-(2'-pyridyl)-*s*-tetrazine (**17**) to give *x*-[^{14}C]-tetrafluoronaphthalene (x-[^{14}C]-**21**) and *x*-[^{14}C]-3,6-di-(2'-pyridyl)pyridazine (x-[^{14}C]-**16**) (Table 2). The unhalogenated *x*-[^{14}C]-benzobarrelenone (x-[^{14}C]-**13**) was degraded as described above for tetrachlorobenzobarrelenone (in Scheme 4) to acetophenone (**9**), which again

was characterised as its oxime (**12**)[10] and was not significantly radioactive. The naphthalene that was produced was converted *via* reaction with tetrachlorobenzyne and then with di-2'-pyridyl-*s*-tetrazine (**17**) into *x*-[^{14}C]-1,2,3,4-tetrachloroanthracene (x-[^{14}C]-**15**), and *x*-[^{14}C]-3,6-di-(2'-pyridyl)pyridazine (x-[^{14}C]-**16**) (Table 2).



Scheme 7

The results collected in Table 2 and expressed as % reaction by routes (a) and (b) in Table 3 show that the proportion of rearrangement occurring by pathway (a) [Scheme 1], that is by aryl migration, increases modestly as the substitution varies from F_4 through Cl_4 to H_4 (no substituent). This is unremarkable since other similar systems[2l,12a] show similar effects, which presumably reflect the need to delocalise positive charge in the transition state for rearrangement. However, the trend is not very pronounced and this may indicate partition of the cation manifold into a more substitution-sensitive component, such as phenonium ion bridging, and a less substitution-sensitive component, such as formation and solvolysis of bisulphate esters. In similar systems the relative orientation of the ester and the migrating bond is known[2d,2e,2k,2m,3d] to be the factor controlling the course of the rearrangement. We have already shown[3d] that solvolysis of both the *exo*- and the *endo*-tosylates (**23**) and (**24**) respectively leads to tetrafluorobenzobarrelenone (**2**) in high yield. The *endo*-tosylate (**24**) solvolyses by etheno-bridge migration to give a cationic species that may be trapped in trifluoroacetic acid to give a mixture of the epimers (**25**) but the *exo*-tosylate (**23**) solvolyses directly to tetrafluorobenzobarrelenone (**2**). These results very strongly support the idea of stereoelectronic control of bond migration in this system.



Rearrangements at *C*-4: effect of acid strength

4-[^{14}C]-1-Methoxytetrafluorobenzobarrelene (4-[^{14}C]-**1**), 4-[^{14}C]-1-methoxytetrachlorobenzobarrelene (4-[^{14}C]-**5**), and 4-[^{14}C]-1-methoxybenzobarrelene (4-[^{14}C]-**18**) were each subjected to acid-catalysed rearrangement at 80°C in 80% sulphuric acid. The *x*-[^{14}C]-tetrafluorobenzobarrelenone (x-[^{14}C]-**2**), *x*-[^{14}C]tetrachlorobenzobarrelenone (x-[^{14}C]-**6**), and *x*-[^{14}C]-benzobarrelenone (x-[^{14}C]-**19**) produced respectively were degraded by the methods described above (Schemes 5,6 and 7). These results are also collected in Tables 2 and 3; the degradation products of the *x*-[^{14}C]-benzobarrelenone (x-[^{14}C]-**19**) produced in 80% sulphuric acid could not be satisfactorily isolated and purified and so no results are reported for this section of the work. The results of rearrangement in 80% sulphuric acid are broadly similar to those obtained for rearrangement in concentrated sulphuric acid. There appears to be less of a preference for rearrangement by aryl migration in the more nucleophilic medium, which may reflect increased competition for incipient carbenium ions by solvent, when the rearrangement pathway would then be determined by the stereochemistry of the intermediate so formed. The previously observed effect of aryl substitution on the rearrangement pathway is also supported by results in 80% sulphuric acid.

Table 3.

Partition between the two pathways (a) and (b) of the rearrangement of the 4-[^{14}C]-1-methoxybenzobarrelenes 4-[^{14}C]-**1**, 4-[^{14}C]-**5**, and 4-[^{14}C]-**18** in sulfuric acid

Compound Number	Compound Name	Conc. sulfuric acid Pathway %		80% sulfuric acid Pathway %	
		a	b	a	b
4-[^{14}C]-**1**	4-[^{14}C]-1-Methoxytetrafluorobenzobarrelene	76	24	68	32
4-[^{14}C]-**5**	4-[^{14}C]-1-Methoxytetrachlorobenzobarrelene	91	9	84	16
4-[^{14}C]-**18**	4-[^{14}C]-1-Methoxybenzobarrelene	95	5	–[a]	–[a]

[a] Results not available

Concluding Comments

The results obtained using [^{14}C]-labelling confirm and extend the results of our previous [^{2}H]-labelling study.[3d] The new results fit within the previously advanced mechanistic scheme (Scheme 1) in which the skeletal rearrangement is doubly degenerate; not only does one bicyclo[2.2.2]octyl system lead to another, it does so by two distinguishable pathways. We have now shown that both of these routes result in the migration of the benzobarrelene *C*-1 to become the benzobarrelenone *C*-2. We have also shown that the mechanistic dichotomy that causes the *C*-4 of the tetrafluorobenzo-series to partition between the *C*-4 and *C*-5 of the product benzobarrelenone is shared by the tetrachlorobenzo- and simple benzo-derivatives. The trend for greater electron withdrawal to lead to less aryl migration is consistent with aryl involvement in the transition state. Although the trend is modest, suggesting little bridging phenonium ion character for pathway (a) (aryl migration) it must be remembered that pathway (b) (etheno-bridge) migration will proceed through a transition

state with benzylic carbenium ion character so that the observed effect is likely to be the balance between two opposing trends. The true extent of benzo-ring involvment in the transition state for pathway (a) would be revealed by detailed kinetic studies of product formation and equilibration (cf. Tanida and coworkers[2d,2e]), although it is not uncommon to see apparently modest kinetic evidence for bridging phenonium ion character even when the circumstantial evidence of product distribution strongly supports aryl participation (the so-called "rate-product quandary").[12] The trends observed with aqueous 80% sulphuric acid are broadly similar, suggesting no dramatic mechanistic differences but rather an understandably increased competition between a more nucleophilic solvent and the internal nucleophiles for the initially formed cation and hence for control of the transition states leading to product control. These results are consistent with the wider set of extensive skeletal rearrangements available to bicyclo-octadienyl cations,[13] which is greatly restricted in this case by the benzo-ring, the relatively high energy of many of the secondary cations that would be involved, and the relatively high stability of the oxycarbenium ion that diverts the rearrangement towards the formation of benzobarrelenones, the observed products. We will report in subsequent papers on some of the more extensive rearrangements that more fully probe the range of the benzobicyclo-octadienyl cation manifold.

Acknowledgements.

We thank the E.P.S.R.C. (formerly S.R.C.and S.E.R.C.) for research studentships to N.J.H. and J.H.H. We also thank the Imperial Smelting Corporation, Avonmouth, for supplies of bromopentafluorobenzene.

Experimental

General Procedures

As described previously[3d,5,6,8] for unlabelled compounds. Radioactive compounds were purified to constant activity by the methods previously described. The radiochemical products were diluted with non-radioactive material wherever necessary or convenient to facilitate isolation or to make supplies last longer. Radioactivities were determined for dilute solutions of the sample (*ca.* 1 mg) in DMF (0.2 mL) and scintillator (5 mL) using a Beckman Instruments CPM-100 liquid scintillation spectrometer. The scintillator was a solution of 2,5-diphenyloxazole (0.38%) and 1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene (0.02%) in toluene. The efficiency of the scintillator was determined using [^{14}C]hexadecane of known specific activity (obtained from the then Radiochemical Centre, Amersham) as standard.

Preparation of 1-[^{14}C]- and 4-[^{14}C]-1,4-Dihydro-1-methoxy-1,4-ethenonaphthalenes (1-Methoxybenzobarrelenes) (4-[^{14}C]-1), (4-[^{14}C]-5), (4-[^{14}C]-18), and (1-[^{14}C]-5) 1-[^{14}C]-5,6,7,8-Tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene (1-[^{14}C]-1-Methoxytetrachlorobenzobarrelene)[7] (1-[^{14}C]-5)

A suspension of 2-carboxytetrachlorobenzenediazonium chloride[7,14] (4.0 g, 12.4 mmole) in a mixture of 1-[^{14}C]anisole[8] (2.05 g, 19.0 mmole) and dry carbon tetrachloride (25 mL) was heated under reflux for 40 min. The solvents were evaporated under reduced pressure (***caution: trap radioactive volatiles***) and the residue was purified by column chromatography on silica-gel to give 1-[^{14}C]-5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene[7] (1-[^{14}C]-**5**) (1.58 g, 26% based on anisole), which was characterised by

direct comparison with our authentic sample; and 2-[^{14}C]-5,6,7,8-tetrachloro-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one[7] (2-[^{14}C]-**6**) (0.114 g, 2% based on anisole), which was also characterised by direct comparison with our authentic sample.

4-[^{14}C]-5,6,7,8-Tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene (4-[^{14}C]-1-Methoxytetrachlorobenzobarrelene)[7] (4-[^{14}C]-5)

The reaction was carried out under the standard conditions[11a] scaled to hexachlorobenzene (28.5 g, 100 mmole)and using 4-[^{14}C]anisole[8] (8.0 g, 74.1 mmole). The reaction mixture was quenched with solid ammonium chloride, filtered, and stripped of volatiles under reduced pressure (***caution: trap radioactive volatiles***). 4-[^{14}C]Anisole was recovered from the volatiles by distillation and then recycled on half of the scale described above. The involatile residue was purified by column chromatography on silica-gel to give 4-[^{14}C]-5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene[7] (1-[^{14}C]-**5**) (1.94 g, 8.1% based on anisole) which was characterised by direct comparison with our authentic sample. A further sample (7.5 g) of very impure material was obtained, which was reductively dechlorinated.[6,11]

4-[^{14}C]-1,4-Dihydro-1-methoxy-1,4-ethenonaphthalene (4-[^{14}C]-1-Methoxybenzobarrelene)[11] (1-[^{14}C]-18)

The very impure sample of 4-[^{14}C]-5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene (4-[^{14}C]-**5**) (7.5 g; contaminated with other chlorohydrocarbons) was reductively dechlorinated[6,11] to give 4-[^{14}C]-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene[11] (4-[14C]-**18**) (1.2 g, 8.8% overall based on anisole), which was characterised by direct comparison with our authentic sample.

4-[^{14}C]-5,6,7,8-Tetrafluoro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalenes (4-[^{14}C]-1-Methoxytetrafluorobenzobarrelene)[7] (4-[^{14}C]-15)

A mixture of bromopentafluorobenzene (5.0 g, 20.2 mmole) and ether (20 mL) was added to stirred magnesium turnings at such a rate that the reaction mixture boiled under gentle reflux. The reaction mixture was then maintained at this temperature for 45 min. A mixture of 4-[^{14}C]anisole[8] (4.0 g, 37.0 mmole) and cyclohexane (15 mL) was added dropwise to the boiling reaction mixture, which was then heated under reflux for 3 h. The reaction mixture was quenched with dilute hydrochloric acid (1 *N*; 20 mL) and extracted with ether (4 x 50 mL). The combined ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure (***caution: trap radioactive volatiles***). The residual red oil was purified by column chromatography on alumina. Elution with light petroleum (b.p. 40 - 60°C) first gave recovered 4-[^{14}C]anisole followed by the 4-[^{14}C]-5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene[7] (4-[^{14}C]-**15**). The recovered 4-[^{14}C]anisole was recycled twice through the reaction described above to give additional 4-[^{14}C]-5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene[7] (4-[^{14}C]-**1**) (total 1.32 g, 13.9% based on anisole), which was characterised by direct comparison with our authentic sample.

General Method for the Rearrangement of [^{14}C]-1-methoxybenzobarrelenes

(a) In concentrated sulphuric acid

A suspension of the dry, powdered [^{14}C]-1-methoxybenzobarrelene in concentrated sulphuric acid (98%; *ca.* 20 mL/g) was shaken at room temperature for *t* min. (Table 4). The resultant solution was poured onto ice

(*ca.* 100 g/g) and the precipitated product was either a) isolated by filtration, washed with water until neutral, and air-dried; or b) extracted thoroughly into ether, which was then washed with water, dried ($MgSO_4$), and carefully evaporated under reduced pressure (*caution: benzobarrelenone and its tetrafluoro-derivative are appreciably volatile and may sublime under even modest vacuum*). The crude product was then purified by preparative t.l.c. [silica-gel; 30% ether in light petroleum (b.p. 40-60°C)]. The trace amounts of other rearrangement products[3d] were not isolated.

(b) In 80% sulphuric acid at 80°C

A suspension of the [^{14}C]-1-methoxybenzobarrelene in hot sulphuric acid [80%, prepared by preheating to 80°C a mixture of concentrated sulphuric acid (4 volumes) and water (1 volume); *ca.* 20 mL/g] was shaken at water-bath temperature (80°C) for *t* min. (Table 4). The resultant solution was poured onto ice (*ca.* 100 g/g) and the benzobarrelenone was isolated as described above.

Table 4.

Rearrangement reaction times t in sulfuric acid for the [14C]-1-methoxybenzobarrelenes 4-[^{14}C]-**1**, 1-[^{14}C]-**5**, 4-[^{14}C]-**5**, and 4-[^{14}C]-**18**

Compound Number	Comopund Name	Rearrangement Reaction time (min)	
		Conc. Sulfuric acid	80% sulfuric acid
1-[14C]-**5**	1-Methoxytetrachlorobenzobarrelene	3	–
4-[14C]-**5**	1-Methoxytetrachlorobenzobarrelene	8	80
4-[14C]-**18**	1-Methoxybenzobarrelene	2	2
4-[14C]-**1**	1-Methoxytetrafluorobenzobarrelene	3	3

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