Rearrangement Reactions of Bicyclic Systems. Part III.[1] Acid-catalysed Rearrangements of 1,4-Dihydro-1-methoxy-1,4-ethenonaphthalene (1-Methoxybenzobarrelene) and its 5,6,7,8-Tetrahalogeno-derivatives

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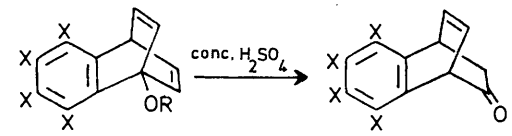
Rearrangements of the title compounds in sulphuric acid gave mixtures of isomeric ketones of structural types (4) [3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one], (7) (5,8-dihydro-5,8-methanobenzocyclohepten-9-one), and (10) (5,9-dihydro-5,9-methanobenzocyclohepten-6-one). The mechanisms of the reactions have been clarified by studies in deuteriosulphuric acid and by using specifically deuteriated substrates. The compounds of type (4) arise by two independent pathways from a C-3 cation, and those of type (7) and (8) arise from a C-2 cation. The products do not arise from an equilibrating series of cations. The mechanistic interpretation is supported by the results of solvolysis studies with a series of toluene-*p*-sulphonates and rearrangements of methyl-substituted 1-methoxybenzobarrelenes.

REARRANGEMENTS of bicyclic molecules have been studied in considerable detail. Among these, acid-catalysed reactions have become a wide area of study as a result of the large number of skeletal changes that are possible.[2] The rearrangement reactions of benzo- and dibenzo-bicyclic systems have been studied in depth,[3] but no results of studies in which a methoxy-group was used as an internal nucleophile had been reported prior to our preliminary communication.[4] Identical studies appeared[5] simultaneously, and an alternative entry into the rearrangement system has also been published.[6]

As a result of our study of the rearrangement reactions of 1-dimethylaminobenzobarrelenes,[1,7] we thought that the analogous methoxy-compounds would have a directing influence on rearrangement reactions. These reactions would be potentially useful as a method of synthesis of compounds which are difficult to obtain by other methods.[8] We now report our results on the acid-catalysed rearrangement reactions of 1-methoxybenzobarrelene (1) and the tetrafluoro- (2) and tetrachloro- (3) analogues. These compounds, particularly the tetrahalogeno-derivatives, are readily available from the reactions of arynes with anisole.[9] Compound (1) was in fact isolated in only 1·5% yield from the decomposition of benzenediazonium-2-carboxylate in the presence of an excess of anisole. We are therefore now studying methods of dechlorinating compounds such as (3).

The choice of media was determined by preliminary experiments which showed that rearrangements only occurred in the presence of strong mineral acids. In concentrated sulphuric acid at room temperature reaction occurred extremely rapidly and no starting material was recovered when reaction mixtures were quenched by pouring onto ice immediately after dissolution. In each of three reactions we obtained three isomeric ketones (Scheme 1). The major product in each case was the corresponding benzobarrelenone [(4)—(6)], isolated in yields varying from 50 to 76%. The minor products were (7)—(9), isolated in 3—8% yields and (10)—(12), isolated in 4·5—6·5% yields.



(1) X = H, R = Me
(2) X = F, R = Me
(3) X = Cl, R = Me
(25) X = F, R = H

(4) X = H
(5) X = F
(6) X = Cl

(7) X = H
(8) X = F
(9) X = Cl

(10) X = H
(11) X = F
(12) X = Cl

SCHEME 1

The structures of the major products (4)—(6) were established by comparison with authentic samples or authentic spectra.† The structures of the other isomeric ketones were established from elemental analyses and spectral data and from the results of hydrogenation over palladium. Thus for example com-

† We thank Professor H. E. Zimmerman for spectra of compound (4).

[1] Part II, H. Heaney and S. V. Ley, *J.C.S. Perkin I*, preceding paper.

[2] J. A. Berson in ' Molecular Rearrangements,' ed. P. de Mayo, vol. 1, Interscience, New York, 1963; A. Fry in ' Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, vol. 4, Wiley–Interscience, New York, 1971; P. D. Bartlett, ' Non-classical Ions,' Benjamin, New York, 1965; S. Winstein, *Quart. Rev.*, 1969, **23**, 141; D. Bethell and V. Gold, ' Carbonium Ions—An Introduction,' Academic Press, London, 1967; G. Olah and P. von R. Schleyer, ' Carbonium Ions,' Interscience, London, 1968.

[3] See for example H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1967, **89**, 3212; S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, 1965, **87**, 2879; P. T. Lansbury and N. T. Boggs, *Chem. Comm.*, 1967, 1007; S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, 1963, **85**, 2675; A. C. G. Gray and H. Hart, *ibid.*, 1968, **90**, 2569; T. P. Lobanova, E. I. Berus, and V. A. Barkhash, *J. Gen. Chem.* (*U.S.S.R.*), 1969, **39**, 2269; S. J. Cristol and M. A. Imhoff, *J. Org. Chem.*, 1971, **36**, 1849; N. M. Povolotskaya, A. Yu. Sheinman, B. G. Derendyaev, M. I. Kollgova, and V. A. Barkhash, *J. Org. Chem.* (*U.S.S.R.*), 1971, **7**, 767.

[4] H. Heaney and S. V. Ley, *Chem. Comm.*, 1971, 225.

[5] I. F. Mikailova and V. A. Barkhash, *J. Org. Chem.* (*U.S.S.R.*), 1970, **6**, 2335.

[6] H. Hart and G. M. Love, *Tetrahedron Letters*, 1971, 2267.

[7] H. Heaney and S. V. Ley, *Chem. Comm.*, 1970, 1184.

[8] H. Heaney, J. H. Hollinshead, G. W. Kirby, S. V. Ley, R. P. Sharma, and K. W. Bentley, *J.C.S. Perkin I*, 1973, 1840.

[9] P. C. Buxton, N. J. Hales, B. Hankinson, H. Heaney, S. V. Ley, and R. P. Sharma, *J.C.S. Perkin I*, 1974, 2681.

pound (8) showed a carbonyl i.r. stretching frequency (1708 cm^{-1}) typical of a polyfluoroaryl ketone [10] which was unchanged in its dihydro-derivative (13). The ^1H n.m.r. spectrum was as expected for a compound of type (8). The i.r. spectra of the compound (11) and its dihydro-derivative (14) showed carbonyl stretching frequencies at 1690 and 1725 cm^{-1}, respectively.

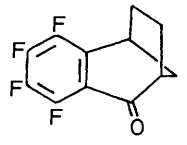
When the rearrangement of the benzobarrelene (2) was carried out in fluorosulphonic acid the crude product, obtained in almost quantitative yield, was shown, by g.l.c. and ^1H n.m.r. spectroscopy, to contain less than 4% of the compounds (8) and (11). The benzobarrelenone (5) was isolated in 90% yield.

We were interested in finding mechanisms which could account for the formation of the three types of ketonic product. It seemed reasonable that the sulphuric acid could protonate one of the double bonds and that the methoxy-group would direct the rearrangement. Rearrangements of this type are known in simpler systems.[11] We proposed to test this hypothesis by carrying out solvolyses of tosylates, which were prepared in the usual way by reduction of the ketone (15) with lithium aluminium hydride to afford the alcohols (16) and (17) and hence the tosylates (18) and (19).

Heating the *exo*-tosylate (18) under reflux in trifluoroacetic acid gave a 98% yield of the ketone (11), but in ethanolic acid solution compound (21), the product of Michael addition to the αβ-unsaturated ketone (11), was obtained. In concentrated sulphuric acid the *exo*-tosylate (18) gave the ketone (11) in 37% yield. In none of these solvolysis reactions did we detect either of the ketones (5) and (8).

The *endo*-tosylate (19) similarly underwent stereospecific rearrangement to the ketone (8). Thus in glacial acetic acid containing sodium acetate and acetic anhydride the compound (8) was obtained in 92% yield. Related 1,2-ethenyl migrations have been reported previously.[12] The stereospecific solvolyses of compounds (18) and (19) suggest the intermediacy of bridged ions such as (20) and (22). Some evidence in favour of the bridged ion (22) was obtained when an experiment was terminated after a short reaction time. The acetate (23) was isolated and its stereochemistry shown by conversion into the *endo*-alcohol (17). Thus the formation of the two minor product types from a cation of type (24) appears reasonable. However, the formation of the benzobarrelenones (4)—(6) in concentrated sulphuric acid is more complex, and a number of mechanistic schemes appeared to be possible. Since the compounds of types (7) and (10) were isolated in low yield it was initially thought that methoxonium salts related to these ketones might be intermediates which lead to compounds of type (4).

We therefore carried out the rearrangement of the 1-hydroxytetrafluorobenzobarrelene (25) in sulphuric acid and obtained the ketones (5), (8), and (11) in 31, 6, and 4·5% yields. We have also tested the various mechanistic pathways by the use of deuteriated solvents and deuteriated starting materials as well as by attempting to equilibrate the various products.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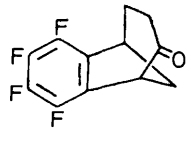
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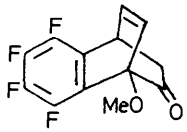
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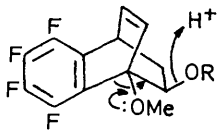
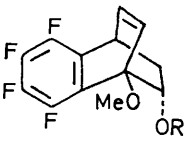
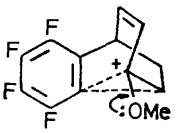

(16) R=H
(18) R=*p*-$MeC_6H_4SO_2$


(17) R=H
(19) R=*p*-$MeC_6H_4SO_2$
(23) R=Ac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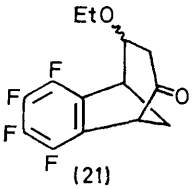
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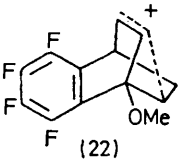
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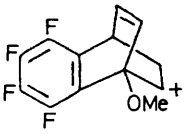
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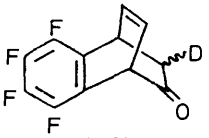
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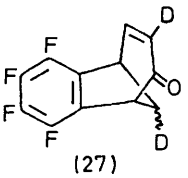
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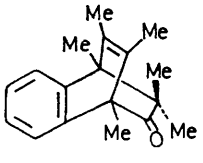

(28)

Dissolution of compound (2) in D_2SO_4–D_2O (80% v/v) at 80° gave deuteriated products [(26) and (27)] which corresponded to compounds (5) and (11). Compound (26) was shown, by mass spectrometry, to contain only one deuterium atom, located in the methylene group. The major fragmentation pathway of molecular ions of this type of compound involves the loss of keten.[9] The

[10] J. K. Brown and K. J. Morgan, in 'Advances in Fluorine Chemistry,' eds. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1965.

[11] K. L. Rabone and N. A. J. Rogers, *Chem. and Ind.*, 1965, 1838; P. H. Boyle, W. Cocker, D. H. Grayson, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1971, 1073.

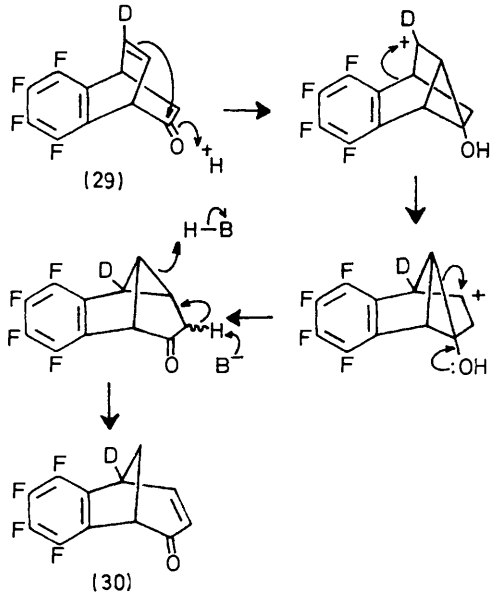
[12] R. L. Cargill and J. W. Crawford, *Tetrahedron Letters*, 1967, 169.

^{1}H n.m.r. spectrum confirmed this result and gave an *exo* : *endo* ratio for deuterium of 10 : 7. In order to be certain that no deuterium was present at any other position we carried out the photolysis [9] of the [^{2}H]benzobarrelenone (26). The 1,2,3,4-tetrafluoronaphthalene thus obtained contained no deuterium. Barkhash [5] obtained similar results and showed that the benzobarrelenone did not undergo deuterium exchange in acid solution. The product (27) was shown to contain two deuterium atoms as indicated. From our previous arguments we expected to find the incorporation of only one deuterium atom, in the methylene group. However, we showed that the vinylic exchange occurred with compound (11) and 80% D_2SO_4–D_2O but not with concentrated D_2SO_4. Exchange α to the carbonyl group seems reasonable in view of the known ease of Michael addition reactions as exemplified by the formation of the ethanol adduct (21). A similar exchange reaction in phenalenone has been reported recently.[13]

Hart has shown [6] that the related ketone (28) can be equilibrated in trifluoroacetic acid with three isomeric ketones, two of which are analogues of our ketones (7) and (10). Before we are able to discuss the mechanism of formation of the compounds (4)—(6) it is appropriate to discuss our attempted equilibration reactions. First, the ketone (8) was heated under reflux in trifluoroacetic acid for 5 days, after which g.l.c., t.l.c., and ^{1}H n.m.r. spectroscopy all showed that no isomerisation to other ketones had occurred. A similar result was obtained with the ketone (11), and with the benzobarrelenone (5) no isomerisation was observed after 30 days. In concentrated sulphuric acid the ketone (8) was not isomerised after 1 h (*ca.* 30 times the normal reaction time) and the ketones (5) and (11) were unchanged after 3 h.

Some idea of the reluctance of the ketones (5), (8), and (11) to undergo interconversion was obtained from treatment of the compounds with concentrated sulphuric acid for an extended period. Compound (11) was recovered almost quantitatively after 8 days. After a similar period the ketone (8) was considerably degraded; however, there was no indication that either of the other ketones had been formed. Compound (5) did react and after 9 days we recovered 11% of starting material together with a 23% yield of the ketone (11). When the [^{2}H]benzobarrelenone (29) was treated with concentrated sulphuric acid for 8 days, starting material was recovered (^{1}H n.m.r. spectroscopy) in 10% yield and the ketone (30) was also isolated, in 22% yield. Mass spectrometry indicated that the deuteriation level was unchanged and ^{1}H n.m.r. spectroscopy showed the position of the deuterium. These results suggest that the benzobarrelenones (4)—(6) are not formed from either the aryl ketones (7)—(9) or the αβ-unsaturated ketones (10)—(12). Further the compounds of types (8) and (11) are not equilibrated *via* a common intermediate.

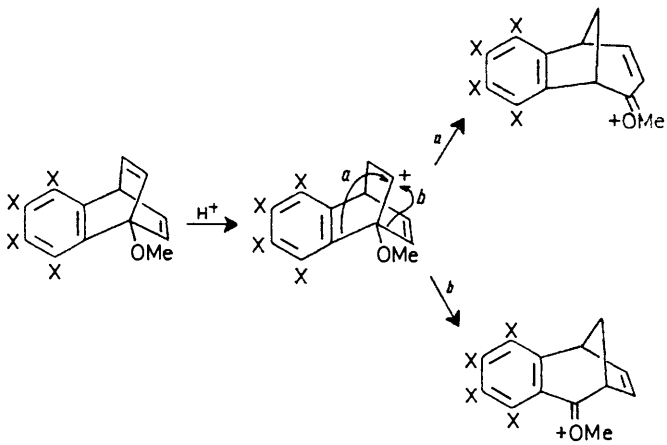
The conversion of the benzobarrelenone (29) into the αβ-unsaturated ketone (30) strongly implies the involvement of the carbonyl group in this slow rearrangement. A number of mechanistic schemes appear reasonable and



SCHEME 2

at present we favour that shown in Scheme 2. We also attempted to equilibrate the ketones (13) and (14). However, they were each recovered unchanged after being heated under reflux in trifluoroacetic acid for 18 h and also when kept in concentrated sulphuric or fluorosulphonic acid at room temperature for 18 and 20 h, respectively. These results are of interest in view of related acid-catalysed interconversions.[14]

Our results suggest that the minor products obtained in the rearrangement reactions of 1-methoxybenzobarrelenes result from initial protonation at position 3 in accord with Scheme 3.



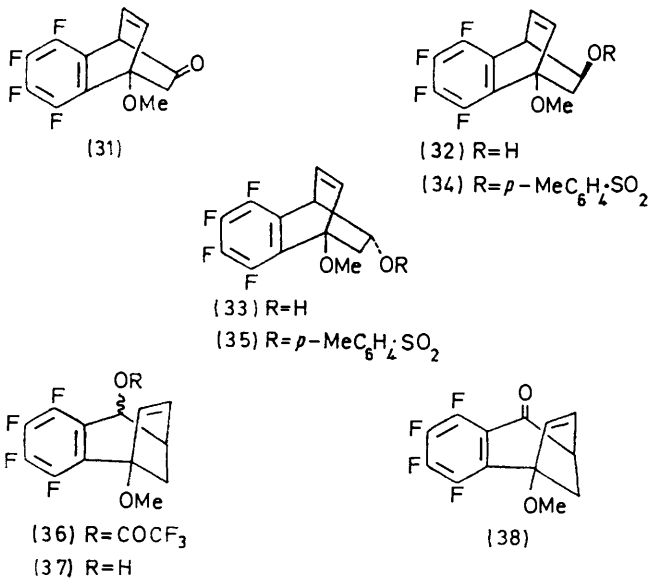
SCHEME 3 X = H, Cl, or F

Since the benzobarrelenones (4)—(6) are evidently not derived from the other isomeric ketones we must con-

[13] A. A. El-Anani, C. C. Greig, and C. D. Johnson, *Chem. Comm.*, 1970, 1024.

[14] M. Laing, P. Sommerville, D. Hanonskova, K. H. Pegel, L. P. L. Piacenza, L. Phillips, and E. S. Waight, *J.C.S. Chem. Comm.*, 1972, 196.

sider other independent routes to account for their formation. Protonation of 1-methoxybenzobarrelenes at position 2 is equally likely. Indeed in a strongly acidic medium when the methoxy-group is also likely to

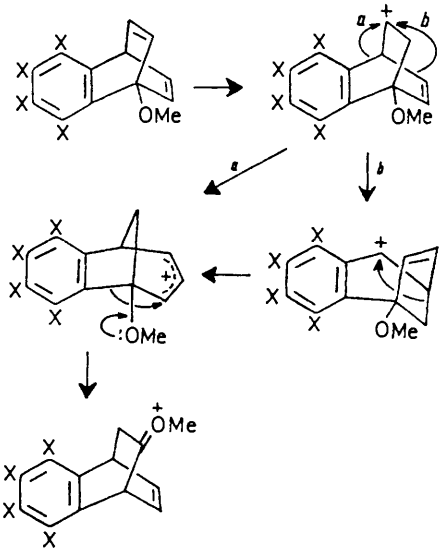


exist predominantly in the protonated form the addition of a second proton is more likely to occur at position 2 since this would give the maximum separation of the two positive charges.

Reduction of the benzobarrelenone (31) with lithium aluminium hydride gave the epimeric alcohols (32) and (33), which were then converted into the *p*-tolylsulphonyl derivatives (34) and (35). In concentrated sulphuric acid the *exo*-toluene-*p*-sulphonate (34) and the *endo*-epimer (35) both gave the benzobarrelenone (5) in 71 and 60% yield, respectively. However, in the more nucleophilic solvent trifluoroacetic acid, although the *exo*-compound (34) gave the ketone (5) in 92% yield, the *endo*-isomer (35) gave an epimeric mixture of the trifluoroacetates (36) under identical conditions. The epimeric trifluoroacetates were characterised by hydrolysis to the alcohols (37), which on oxidation with chromic oxide in pyridine gave the ketone (38), readily identified by elemental analysis and spectral data. It is significant that the alcohols (37) gave the benzobarrelenone (5) in concentrated sulphuric acid. This series of transformations suggests that the major products formed in the acid-catalysed rearrangements of 1-methoxybenzobarrelenes can arise by two independent routes as shown in Scheme 4. The ketones (8) and (11) were not present amongst the products of any of the reactions of compounds (34) and (35). Participation of the ion which results from the initial protonation at position 2 (Scheme 4) was implicated when a reaction of compound (2) was carried out in sulphuric acid–water (2 : 1 v/v), which gave, among other products, the alcohol (32).

The most reliable insight into the mechanisms of these reactions can be obtained by using isotopically labelled compounds. We are at present investigating the reactions of 1-methoxy[1-^{14}C]tetrachlorobenzobarrelene and its tetrafluoro-[4-^{14}C]-analogue, and now report the results of reactions with specifically deuteriated compounds. We prepared compounds (39)—(41) by the reactions of tetrafluorobenzyne with the appropriate deuteriated anisoles.

The methods of preparing deuteriated phenols and hence anisoles usually involve exchange reactions.[15] Thus [2,4,6-$^2H_3$]phenol (90% $^2H_3$, 10% $^2H_2$) has been prepared [16] from sodium phenolate and deuterium oxide. These methods use a large excess of deuterium oxide. We prepared deuteriated anisoles by the deuteriolysis of organometallic reagents. Thus addition of deuterium oxide to *p*-methoxyphenylmagnesium bromide gave [4-^{2}H]anisole (87% ^{2}H, 13% ^{1}H). [2,4,6-$^2H_3$]Anisole was prepared in two steps from 2,4,6-tribromoanisole. The reaction of n-butyl-lithium with 2,4,6-tribromoanisole in light petroleum [17] gave after deuteriolysis 4-bromo[2,6-$^2H_2$]anisole, which on reaction with n-butyl-lithium in ether [18] followed by treatment with deuterium oxide gave [2,4,6-$^2H_3$]anisole. Mass spectrometry showed that the deuterium incorporation was



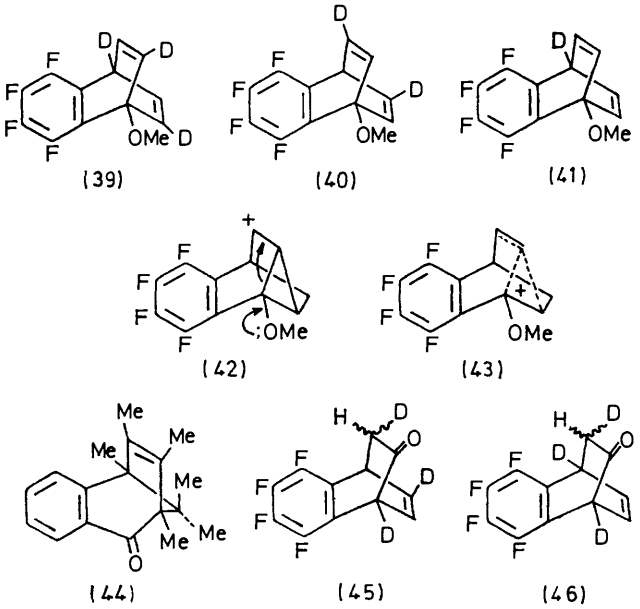
SCHEME 4 X = H, Cl, or F

>99% $^2H_3$. We prepared [3,5-$^2H_2$]anisole from 1,3,5-tribromobenzene. Bromo[3,5-$^2H_2$]benzene has been prepared previously both from [$^2H_6$]benzene [19] and *via* 1,3,5-tribromobenzene by deuteriolysis of a Grignard reagent.[20] We prepared bromo[3,5-$^2H_2$]benzene by step-

[15] A. F. Thomas, 'Deuterium Labelling in Organic Chemistry,' Appleton Century Crofts, New York, 1971.
[16] D. H. Williams, S. W. Tam, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 2150.
[17] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.
[18] H. Gilman, W. Langham, and H. B. Willis, *J. Amer. Chem. Soc.*, 1940, **62**, 346.
[19] D. F. Evans and G. V. Fazakerley, *J. Chem. Soc.* (*A*), 1971, 184.
[20] G. Fraenkel, D. G. Adams, and R. R. Dean, *J. Phys. Chem.*, 1968, **72**, 944.

wise replacement of two of the bromine atoms in 1,3,5-tribromobenzene with n-butyl-lithium in ether.[17,21] The [$^2H_2$]bromobenzene was converted into [3,5-$^2H_2$]-phenol by a Grignard reaction (to give [3,5-$^2H_2$]phenyl dimethyl borate) followed by oxidation with hydrogen peroxide.[22] Methylation in dimethyl sulphoxide [23] gave the required anisole (77% $^2H_2$, 19% ^2H, 4% ^1H).

Rearrangements of the compounds (39)—(41) in concentrated sulphuric acid gave deuteriated products corresponding to compounds (8) and (11). Mass spectrometry showed that no exchange of deuterium for protium had occurred. ^1H N.m.r. spectroscopy showed a pattern of deuteriation entirely in accord with the mechanism given in Scheme 3. The data for the deuteriated analogues of compounds (8) and (11) are given in Tables 1 and 2. The formation of the αβ-unsaturated ketone could involve the bridged ion (20) and similarly the aryl ketone (8) could arise *via* a cyclopropylcarbinyl cation (42) or the non-classical ion (43). The absence of deuterium scrambling shows that degenerate cyclopropylcarbinyl cations, of the type observed in reactions of compound (44),[24] are not involved in this system. It is not clear whether this is due to the absence of methyl groups or to the presence of the halogen atoms in our compounds. It is noteworthy that the αβ-unsaturated ketone (11) obtained from the reaction of compound (39) with sulphuric



acid–water (80% v/v) at 80° only contained two deuterium atoms, thus confirming the rapid exchange, in the presence of aqueous sulphuric acid, of protons α to the carbonyl group in the ketone (11).

The deuteriated compounds related to tetrafluorobenzobarrelenone (5) were also obtained from the rearrangement reactions of compounds (39)—(41) in concentrated sulphuric acid. In addition, the rearrangement of the compound (39) in sulphuric acid containing water (80% v/v) also gave deuteriated tetrafluorobenzobarrelenone (5). Inspection of Scheme 4 shows that different deuteriation patterns will be obtained according to whether path *a* or *b* is followed. It was therefore important to determine not only the total deuterium content of the tetrafluorobenzobarrelenones, but also the precise location of each deuterium atom. For example, compound (39) would give rise to the [$^2H_3$]tetrafluorobenzobarrelenone (45) by path *a*, whereas path *b* would afford the isomer (46). The compounds (40) and (41) would also afford different products by the two pathways. Mass spectrometry showed that there was, within experimental error, no loss of deuterium during the rearrangement reactions. Replicate integration of the ^1H n.m.r. spectra gave information about the number of protons present at each position in the products. The two bridgehead protons in compound (5) are virtually isochronous (^1H n.m.r. spectrum). However, since it was important to differentiate between the two bridgehead positions, ^1H n.m.r. spectra were taken in the presence of tris-(dipivaloylmethanato)europium.[25] The expected large down-field shift of the resonance due to the bridgehead proton adjacent to the carbonyl group allowed the

TABLE 1

^1H N.m.r. data (τ values) for compounds of type (8) obtained from rearrangements of the compounds (39)—(41) in sulphuric acid (98%) at room temperature

Source of product	H-5	H-6	H-7	H-8	H-10
(39)			3·35br (1H, s)		7·3—7·48 (2H, q, |*J*| 14 Hz)
(40)	5·7—6·0 (1H, m)	3·8 (1H, d, |*J*| 3·5 Hz)		6·5—6·75 (1H, m)	7·2—7·5 (1H, m)
(41)		3·7—3·9 (1H, q, |*J*| *ca.* 5·5 and 3·5 Hz)	3·25 (1H, m)	6·5—6·7 (1H, m)	7·3—7·6 (2H, m)

TABLE 2

^1H N.m.r. data (τ values) for compounds of type (11) obtained from rearrangements of compounds (39)—(41) in sulphuric acid

Source of product	H-5	H-7	H-8	H-9	H-10
(39) [a]		4·54 (1H, d, |*J*| 10 Hz)	2·65 (1H, d, |*J*| 10 Hz)		7·25br (2H, s)
(39) [b]			2·65br (1H, s)		7·25br (2H, s)
(40) [b]	5·7—6·05 (1H, m)	4·46br (1H, s)		5·7—6·05 (1H, m)	7·23 (1H, m)
(41) [b]	5·8—6·05 (1H, m)	4·5 (1H, q, |*J*| *ca.* 10 and 1·5 Hz)	2·62 (1H, d, |*J*| 10 Hz)		7·2 (2H, m)

[a] In 80% sulphuric acid at 80°. [b] In 98% sulphuric acid at room temperature.

expected large down-field shift of the resonance due to the bridgehead proton adjacent to the carbonyl group allowed the

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required analysis. The percentages of reactions by paths *a* and *b* (Scheme 4) which gave the best fit with the ^{1}H n.m.r. spectral data are given in Table 3. The results are best accommodated if we assume that in concentrated sulphuric acid *ca.* 80% of compound (5) arises by path *a* and *ca.* 20% by path *b*. In sulphuric acid–water (4 : 1 v/v) at 80° the values obtained were *ca.* 55% for path *a* and *ca.* 45% for path *b*.

TABLE 3

Integration ratios from ^{1}H n.m.r. spectra of compounds of type (5) obtained from rearrangements of compounds (39)—(41) in sulphuric acid

Source of product		Olefinic	Bridgehead	Methylene
(39) [a]	Obs.	2·54	1·0	1·9
	Calc.	2·64	1·0	1·82
(39) [b]	Obs.	1·52	1·0	1·3
	Calc.	1·53	1·0	1·27
(40) [b]	Obs.	1·0	1·3	2·13
	Calc.	1·0	1·35	2·07
(41) [b]	Obs.	1·0	1·32	1·54
	Calc.	1·0	1·37	1·52

[a] In 80% sulphuric acid at 80°. [b] In 98% sulphuric acid at room temperature.

Since the two mechanistic pathways were distinguished largely on the basis of different deuteriation levels at the bridgehead position remote from the carbonyl group and in the ethenyl residue it was important to establish that no scrambling occurred between these two positions under the reaction conditions used. The [^{2}H]tetrafluorobenzobarrelenone (29) was therefore dissolved in concentrated sulphuric acid and was re-isolated after 3 h at room temperature completely unchanged, as indicated by ^{1}H n.m.r. spectroscopy. As an additional check each of the deuteriated tetrafluorobenzobarrelenones was converted into the deuteriated 1,2,3,4-tetrafluoronaphthalene by photolysis.[9] A comparison of the integration values for the numbers of protons at the 5- and 8-positions and at the 6- and 7-positions in the ^{1}H n.m.r. spectra, with those expected from the values in Table 3, is given in Table 4. Good agreement was obtained.

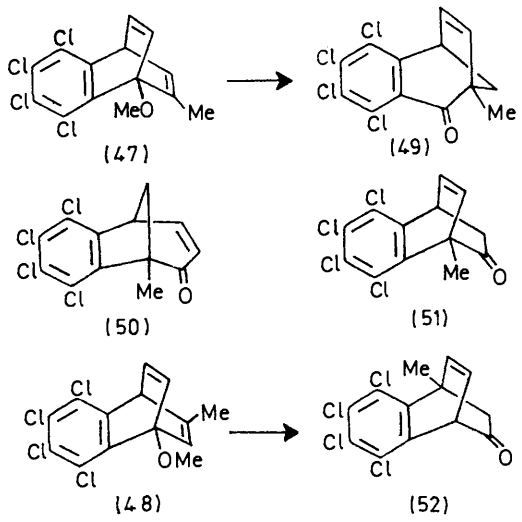
TABLE 4

Integration ratios from ^{1}H n.m.r. spectra of 1,2,3,4-tetrafluoronaphthalene obtained by photolysis of the deuteriated compounds (5) produced from compounds (39)—(41) as in Table 3

Source of product		Proton ratios: 5 and 8	6 and 7
(39) [a]	Obs.	1·0	2·6
	Calc.	1·0	2·64
(39) [b]	Obs.	1·0	1·53
	Calc.	1·0	1·53
(40) [b]	Obs.	1·35	1·0
	Calc.	1·35	1·0
(41) [b]	Obs.	1·33	1·0
	Calc.	1·37	1·0

A number of assumptions have been made in our interpretation, mainly in connection with possible isotope effects. Thus it is assumed that the addition of a deuteron is as easy as that of a proton. Also we have assumed that the orientation of protonation of a double bond is not significantly affected by the presence of deuterium atoms. Other mechanisms have been proposed [5] in order to explain the formation of compound (5) from 1-methoxytetrafluorobenzobarrelene (2). These involve a bridgehead olefin and hydride-ion shifts and can be excluded by our results. ^{14}C-Labelling studies [26] exclude mechanisms which involve 1,2-migration of the methoxy-group. Similar 1,2-hydroxy-shifts are known [27] but the strain present in the benzobarrelene system presumably precludes such rearrangements in the present case.

The results presented suggest that the presence of alkyl groups at suitable positions would polarise the initial protonation and thus direct the rearrangements either in accord with Schemes 3 or 4. Our results obtained with both 2-methyl- (47) and 3-methyl-1-methoxytetrachlorobenzobarrelene (48) support this



SCHEME 5

proposition. Compound (47) rearranged readily in trifluoroacetic acid and gave a mixture of the three ketones (49)—(51) in 56, 40, and 4% yield, respectively (Scheme 5). In concentrated sulphuric acid the ketones (49)—(51) were obtained in 3·5, 27, and 28% yields respectively. These results provide further evidence that in strongly acidic media protonation of the methoxy-group in 1-methoxybenzobarrelenes directs the subsequent addition of a proton to a double bond. The ketone (52) was isolated in quantitative yield from a rearrangement of the 1-methoxybenzobarrelene (48) in trifluoroacetic acid, and in the presence of concentrated sulphuric acid the same product (52) was isolated in 90% yield. Apparently in this particular system the rearrangement according to Scheme 4 only involves path *a*. Further studies are in progress in order to obtain more details concerning the variations which are possible using 1-methoxybenzobarrelenes.

[26] N. J. Hales, H. Heaney, and J. H. Hollinshead, unpublished observations.

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EXPERIMENTAL

General methods used were as given in ref. 28.

Reaction of Benzyne with Anisole.—Benzenediazonium-2-carboxylate [29] [from anthranilic acid (34·2 g)] was added to anisole (300 g) at 45°. The mixture was stirred at this temperature for 18 h and the excess of anisole distilled off under reduced pressure to leave a dark oil. Repeated column chromatography (alumina) gave a number of products which were not fully characterised and also 1,4-*dihydro*-1-*methoxy*-1,4-*ethenonaphthalene* (1) (650 mg, 1·5%), m.p. 37—38° [from light petroleum (b.p. 40—60°)] (Found: C, 84·2; H, 6·3%; M^{+}, 184. $C_{13}H_{12}O$ requires C, 84·7; H, 6·55%; *M*, 184), τ (CCl_4) 2·9—3·5 (8H, m), 5·2—5·5 (1H, m), and 6·28 (3H, s).

Rearrangement of the Ethenonaphthalene (1).—Compound (1) (300 mg) was dissolved in concentrated sulphuric acid (5 ml) by shaking at room temperature for *ca.* 30 s. The solution was poured onto crushed ice (30 g) and then allowed to warm to room temperature. The mixture was extracted with ether (5 × 10 ml) and the combined extracts were washed with water until acid-free, dried, and evaporated to leave an oil which was separated by preparative layer chromatography to afford, in order of decreasing R_F value, (i) 5,8-*dihydro*-5,8-*methanobenzocyclohepten*-9-*one* (7) (22 mg, 8%), an oil (Found: M^{+}, 170·0729. $C_{12}H_{10}O$ requires *M*, 170·0732), τ (CCl_4) 2·05—2·3 (1H, m), 2·6—3·1 (3H, m), 3·3 (1H, dd, $|J|$ *ca.* 5·5 and 3·5 Hz), 3·9 (1H, dd, $|J|$ *ca.* 5·5 and 3·5 Hz), 6·3—6·5 (1H, m), 6·5—6·7 (1H, m), and 7·15—7·6 (2H, m), $\nu_{max.}$ 1697 cm^{-1}; (ii) 3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (4) (139 mg, 50%), m.p. 54—55° (after sublimation) (lit.,[30] 56—58°), τ ($CDCl_3$) 2·55—2·95 (4H, m), 3·05—3·6 (2H, m), 5·57 (1H, q, $|J|$ *ca.* 5·5 and 2·5 Hz), 5·6—5·9 (1H, m), and 7·5—8·3 (2H, octet, AB of ABX, $|J|_{AB}$ 17·5, $|J|_{BX} = |J|_{AX}$ = 2·5 Hz), $\nu_{max.}$ 3080, 3015, 2930, 1735, 1470, 1460, 1410, 1334, 1300, 1145, 1120, 1080, 960, and 687 cm^{-1} (identical with the spectrum of an authentic sample); and (iii) 5,9-*dihydro*-5,9-*methanobenzocyclohepten*-6-*one* (10) (18 mg, 6·5%), m.p. 55° (from hexane) (Found: M^{+}, 170·0732), τ (CCl_4) 2·5—3·1 (5H, m), 4·65 (1H, q, $|J|$ 10·0 and 1·5 Hz), 6·15—6·55 (2H, m), and 7·15—7·4 (2H, m), $\nu_{max.}$ 1680 cm^{-1}, $\lambda_{max.}$ (MeOH) 231 (ε 7450) and 348 nm (196).

Rearrangements of 5,6,7,8-*Tetrafluoro*-1,4-*dihydro*-1-*methoxy*-1,4-*ethenonaphthalene* (2).—(a) *In concentrated sulphuric acid.* Compound (2) (1·5 g), treated as in the previous experiment, gave the following products (isolated by preparative layer chromatography) in order of decreasing R_F value: (i) 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5,8-*methanobenzocyclohepten*-9-*one* (8) (71 mg, 5%), m.p. 82—83° (from ethanol) (Found: C, 59·35; H, 2·7%; M^{+}, 242. $C_{12}H_6F_4O$ requires C, 59·5; H, 2·5%; *M*, 242), τ (CCl_4) 3·3 (1H, q, $|J|$ *ca.* 5·5 and 3·5 Hz), 3·8 (1H, q, $|J|$ *ca.* 5·5 and 3·5 Hz), 5·8—6·05 (1H, m), 6·5—6·8 (1H, m), and 7·1—7·6 (2H, m, $|J|_{AB}$ 14·0 Hz), $\nu_{max.}$ 1708 cm^{-1}, $\lambda_{max.}$ (EtOH) 257 (ε 2100) and 295 nm (940); (ii) 5,6,7,8-tetrafluoro-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (5) (910 mg, 64%), m.p. and mixed m.p. 71—73° (from ethanol) (lit.,[5] 72·5—73·5°), τ (CCl_4) 3·02—3·48 (2H, m), 5·18—5·55 (2H, m), and 7·94 (2H, octet, AB of ABX, $|J|_{AB}$ 17, $|J|_{AX} = |J|_{BX}$ = 2·5 Hz), $\nu_{max.}$ 1738 cm^{-1}; and (iii) 1,2,3,4-*tetrafluoro*-5,9-*dihydro*-5,9-*methanobenzocyclohepten*-6-*one* (11) (69 mg, 5%), m.p. 74—75° (from hexane) (Found: C, 59·6; H, 2·65%; M^{+}, 242), τ (CCl_4) 2·6 (1H, q, $|J|$ 10·3 and 7·0 Hz), 4·55 (1H, q, $|J|$ 10·3 and 1·5 Hz), 5·8—6·2 (2H, m), and 7·1—7·3 (2H, m), $\nu_{max.}$ 1690 cm^{-1}, $\lambda_{max.}$ (EtOH) 222 (ε 7890), 273 (900), and 350 nm (160).

(b) *In aqueous sulphuric acid* (1 : 4 v/v). This gave compounds (5) (66%) and (11) (6%).

(c) *In fluorosulphonic acid.* Fluorosulphonic acid (5 ml) was stirred at −70° and compound (2) (500 mg) was added. The mixture was allowed to warm to 0° and cautiously added to crushed ice (60 g). The white precipitate was washed with water and dried. The aqueous phase was extracted with ether and gave, after the usual work-up, more product. The combined product was found by g.l.c. to be >96% pure. Sublimation gave compound (5) (425 mg, 90%).

(d) *In aqueous sulphuric acid* (1 : 3 v/v). Compound (2) (500 mg) dissolved in aqueous sulphuric acid at 80° was stirred for 15 min and added to ice (50 g). The usual work-up, followed by preparative layer chromatography, gave compounds (8), (5), and (11) in 6, 30, and 4% yields, respectively. A slower running band gave 5,6,7,8-*tetrafluoro*-1,2,3,4-*tetrahydro*-4-*methoxy*-1,4-*ethenonaphthalen*-2-exo-*ol* (32) (92 mg, 17%), m.p. 99—100° (from methanol) (Found: M^{+}, 274·0616. $C_{13}H_{10}F_4O_2$ requires *M*, 274·0617), τ ($CDCl_3$) 3·28 (1H, d, $|J|$ *ca.* 8 Hz), 3·64 (1H, q, $|J|$ *ca.* 8 and 6 Hz), 5·6—6·0 (2H, m), 6·39 (3H, d, $|J|_{H,F}$ 2 Hz), 7·75 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 12, $|J|_{3\text{-}endo,2\text{-}endo}$ 8 Hz), 7·95br (1H, s, exchangeable), and 8·65 (1H, q, $|J|_{3\text{-}endo,3\text{-}exo}$ 12, $|J|_{3\text{-}exo,2\text{-}endo}$ 3 Hz), $\nu_{max.}$ 3450 cm^{-1}.

Rearrangement of 5,6,7,8-*Tetrafluoro*-1,4-*dihydro*-1,4-*ethenonaphthalen*-1-*ol* (25) *in Sulphuric Acid.*—By the foregoing procedure (conc. sulphuric acid) compound (25) [5] gave compounds (5), (8), and (11) in 31, 6, and 4·5% yields, respectively.

Rearrangement of 5,6,7,8-*Tetrachloro*-1,4-*dihydro*-1-*methoxy*-1,4-*ethenonaphthalene* (3) *in Concentrated Sulphuric Acid.*—Compound (3) (952 mg) in concentrated sulphuric acid (25 ml) gave, after conventional work-up and preparative layer chromatography, in order of decreasing R_F value: (i) 1,2,3,4-*tetrachloro*-5,8-*dihydro*-5,8-*methanobenzocyclohepten*-9-*one* (9) (29 mg, 3·2%), m.p. 154—155° (from ethanol) (Found: C, 46·9; H, 2·2. $C_{12}H_6Cl_4O$ requires C, 46·8; H, 1·95%), τ ($CDCl_3$) 3·27 (1H, q, $|J|$ *ca.* 5·5 and 3·5 Hz), 3·77 (1H, q, $|J|$ *ca.* 5·5 and 3·5 Hz), 5·5—5·7 (1H, m), 6·35—6·55 (1H, m), and 7·1—7·6 (2H, m), $\nu_{max.}$ ($CHCl_3$) 1708 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 (ε 7440), 268 (5216), 318 (1830), and 328 nm (1850); (ii) 5,6,7,8-tetrachloro-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (6) (688 mg, 76%), m.p. 166—168° (lit.,[31] 150°); and (iii) 1,2,3,4-*tetrachloro*-5,9-*dihydro*-5,9-*methanobenzocyclohepten*-6-*one* (12) (41 mg, 4·5%), m.p. 144—146° (from hexane–benzene) (Found: C, 46·95; H, 1·95%), τ ($CDCl_3$) 2·54 (1H, q, $|J|$ 10·0 and 7·0 Hz), 4·46 (1H, q, $|J|$ 10·0 and 1·7 Hz), 5·75—6·2 (2H, m), and 7·1—7·3 (2H, m), $\nu_{max.}$ ($CHCl_3$) 1700 and 1680 cm^{-1}, $\lambda_{max.}$ (EtOH) 230 nm (ε 20,200).

Rearrangements of 5,6,7,8-*Tetrachloro*-1,4-*dihydro*-1-*methoxy*-3-*methyl*-1,4-*ethenonaphthalene* (48).—(a) *In trifluoroacetic acid.* A solution of compound (48) (251 mg) in trifluoroacetic acid (25 ml) was heated under reflux for 2 h and the solvent was then removed to leave a tan

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[31] H. Heaney and J. M. Jablonski, *J. Chem. Soc.* (*C*), 1968, 1895.

powder. Preparative layer chromatography gave 5,6,7,8-*tetrachloro*-3,4-*dihydro*-4-*methyl*-1,4-*ethenonaphthalen*-2(1H)-*one* (52) (241 mg, 100%), m.p. 138—140° (from ethanol) (Found: C, 48·6; H, 2·55%; M^+, 322. $C_{13}H_8Cl_4O$ requires C, 48·45; H, 2·5%; *M*, 322), τ ($CDCl_3$) 3·32 (1H, q, $|J|$ *ca.* 7·3 and 6·5 Hz), 3·56 (1H, q, $|J|$ *ca.* 7·3 and 2·0 Hz), 4·95 (1H, q, $|J|$ *ca.* 6·5 and 2·0 Hz), and 7·93 (5H, m), *m/e* 322 (M^+, *ca.* 1%) and 280 (*M* − 42, 100%), $\nu_{max.}$ 1740 cm^{-1}.

(b) *In concentrated sulphuric acid.* Compound (48) (214 mg) was shaken with sulphuric acid (5 ml; 98%) until it dissolved (2·5 min) and then poured onto crushed ice (40 g). The mixture was filtered to afford compound (52) (184 mg, 89·5%), identical (n.m.r., t.l.c., and i.r. spectroscopy) with the foregoing compound.

Rearrangements of 5,6,7,8-*Tetrachloro*-1,4-*dihydro*-1-*methoxy*-2-*methyl*-1,4-*ethenonaphthalene* (47).—(a) *In trifluoroacetic acid.* A solution of compound (47) (181 mg) in trifluoroacetic acid (10 ml) was heated under reflux for 2 h and the solvent was removed to leave an oil. Preparative layer chromatography gave, in order of decreasing R_F value: (i) 1,2,3,4-*tetrachloro*-5,8-*dihydro*-8-*methyl*-5,8-*methanobenzocycloheptene*-9-*one* (49) (98 mg, 56%), m.p. 129—130° (from ethanol) (Found: C, 48·4; H, 2·6%; M^+, 322. $C_{13}H_8Cl_4O$ requires C, 48·45; H, 2·5%; *M*, 322), τ ($CDCl_3$) 3·40 (1H, q, $|J|$ *ca.* 5·0 and 3·5 Hz), 4·14 (1H, d, $|J|$ *ca.* 5 Hz), 5·60 (1H, dt, $|J|$ *ca.* 3·5 and 3·0 Hz), 7·53 (2H, d, $|J|$ *ca.* 3·0 Hz), and 8·60 (3H, s), $\nu_{max.}$ 1710 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 (ε 7100), 270 (4600), 317 (1580), and 326 nm (1547); (ii) 5,6,7,8-*tetrachloro*-3,4-*dihydro*-1-*methyl*-1,4-*ethenonaphthalen*-2(1H)-*one* (51) (7 mg, 4%), m.p. 164—165° (from ethanol) (Found: C, 48·4; H, 2·55%), *m/e* 322 (M^+, 1%) and 280 (*M* − 42, 100%), τ ($CDCl_3$) 3·18 (1H, q, $|J|$ *ca.* 7 Hz), 3·77 (1H, q, $|J|$ *ca.* 7·0 and 1·7 Hz), 5·19 (1H, ddt, $|J|$ *ca.* 7·0, 1·7, and 2·4 Hz), 7·65 (1H, dd, $|J|$ *ca.* 18·2 and 2·4 Hz), 7·89 (1H, dd, $|J|$ *ca.* 18·2 and 2·4 Hz), and 7·95 (3H, s), $\nu_{max.}$ 1735 cm^{-1}; and (iii) 1,2,3,4-*tetrachloro*-5,9-*dihydro*-5-*methyl*-5,9-*methanobenzocyclohepten*-6-*one* (50) (70 mg, 40%), m.p. 140—142° (from ethanol) (Found: C, 48·4; H, 2·55%; M^+, 322), τ ($CDCl_3$) 2·55 (1H, q, $|J|$ *ca.* 9·4 and 6·0 Hz), 4·41 (1H, d, $|J|$ *ca.* 9·4 Hz), 6·01 (1H, m), 7·36 (2H, m), and 8·26 (3H, s), $\nu_{max.}$ 1690 cm^{-1}, $\lambda_{max.}$ (EtOH) 234sh (ε 18,100), 292 (4640), 305 (4300), 339 (2780), 350 (3320), and 359 nm (2450).

(b) *In concentrated sulphuric acid.* By the standard procedure compound (47) gave compounds (49), (51), and (50) in 3·6, 28, and 27% yields, respectively.

Catalytic Reductions.—(*a*) Compound (8) (40 mg) in ethanol (10 ml) with hydrogen in the presence of pre-reduced palladium–carbon gave 1,2,3,4-*tetrafluoro*-5,6,7,8-*tetrahydro*-5,8-*methanobenzocyclohepten*-9-*one* (13) (38 mg, 95%), m.p. 74—75° (from ethanol) (Found: C, 59·05; H, 3·35. $C_{12}H_8F_4O$ requires C, 59·0; H, 3·3%), τ ($CDCl_3$) 6·0—6·4 (1H, m), 6·7—7·0 (1H, m), and 7·4—8·9 (8H, m), $\nu_{max.}$ ($CHCl_3$) 1708 cm^{-1}.

(*b*) Compound (5) similarly gave 1,2,3,4-*tetrafluoro*-5,7,8,9-*tetrahydro*-5,9-*methanobenzocyclohepten*-6-*one* (14), m.p. 80—85° (from hexane) (Found: M^+, 244·0523. $C_{12}H_8F_4O$ requires *M*, 254·0522), τ ($CDCl_3$) 6·0—6·4 (2H, m) and 7·1—8·3 (6H, m), $\nu_{max.}$ ($CHCl_3$) 1725 cm^{-1}.

Reductions of Ketones.—(a) *The ketone* (15). The ketone (15) (2·0 g) in ether (25 ml) was added dropwise to a suspension of lithium aluminium hydride (0·3 g) in ether (25 ml) and the mixture was stirred during 15 min. Standard work-up gave an epimeric mixture of alcohols which were separated by preparative layer chromatography. The upper band gave 5,6,7,8-*tetrafluoro*-1,2,3,4-*tetrahydro*-1-*methoxy*-1,4-*ethenonaphthalen*-2-exo-*ol* (16) (1·1 g, 55%), m.p. 113—115° (from ethanol) (Found: C, 57·05; H, 3·7. $C_{13}H_{10}F_4O_2$ requires C, 56·95; H, 3·7%), τ ($CDCl_3$) 3·2—3·5 (2H, m), 5·6—5·9 (1H, m), 5·9—6·2 (1H, m), 6·27 (3H, d, $|J|_{H,F}$ 3 Hz), 7·12br (1H, s, exchangeable), 8·02 (1H, qd, $|J|$ *3-exo,3-endo ca.* 13, $|J|_{3\text{-}endo,2}$, *ca.* 8, $|J|_{3\text{-}endo,4}$ *ca.* 3 Hz), and 8·64 (1H, dt, $|J|_{3\text{-}exo,3\text{-}endo}$ *ca.* 13, $|J|_{3\text{-}exo,2}$ *ca.* 3, $|J|_{3\text{-}exo,4}$ *ca.* 3 Hz), $\nu_{max.}$ 3530 cm^{-1}. The lower band gave the 2-endo-*ol* (17) (0·73, 37%), m.p. 126—127° (from methanol) (Found: C, 57·0; H, 3·6%), τ ($CDCl_3$) 3·3—3·5 (2H, m), 5·6—5·9 (1H, m), 5·98 (1H, q, $|J|_{2,3\text{-}exo}$ *ca.* 8, $|J|_{2,3\text{-}endo}$ *ca.* 3 Hz), 6·31 (3H, d, $|J|_{H,F}$ 2 Hz), 7·1br (1H, s, exchangeable), 7·88 (1H, qd, $|J|_{3\text{-}exo,3\text{-}endo}$ *ca.* 12·5, $|J|_{3\text{-}exo,2}$ *ca.* 8·5, $|J|_{3\text{-}exo,4}$ *ca.* 3·0 Hz), and 8·87 (1H, dt, $|J|_{3\text{-}exo,3\text{-}endo}$ *ca.* 12·5, $|J|_{3\text{-}endo,4}$ *ca.* 3, $|J|_{3\text{-}endo,2}$ *ca.* 3 Hz), $\nu_{max.}$ 3580 cm^{-1}.

(b) *The ketone* (31). The ketone (31) was reduced with lithium aluminium hydride in the usual way and gave, by preparative layer chromatography, (i) 5,6,7,8-tetrafluoro-1,4-dihydro-4-methoxy-1,4-ethenonaphthalen-2-*exo*-ol (32) (59%), m.p. and mixed m.p. 99—100° (from methanol), identical (t.l.c. and i.r. and ^1H n.m.r. spectroscopy) with material isolated previously; and (ii) the 2-*endo*-ol (33) (39%), an oil, τ ($CDCl_3$) 3·06 (1H, d, $|J|$ *ca.* 8 Hz), 3·49 (1H, q, $|J|$ *ca.* 8 and 6 Hz), 5·4—5·7 (1H, m), 5·7—6·1 (1H, m), 6·35 (3H, d, $|J|_{H,F}$ 2 Hz), 7·67 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 12, $|J|_{3\text{-}exo,2}$ 8 Hz), 7·85br (1H, s, exchangeable), and 8·42 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 12, $|J|_{3\text{-}endo,2}$ 3 Hz), $\nu_{max.}$ 3400br cm^{-1}.

Preparation of p-*Tolylsulphonyl Derivatives.*—The alcohols (16), (17), (32), and (33) were treated as follows. Toluene-*p*-sulphonyl chloride (100 mg) in pyridine (2 ml) was added dropwise to a solution of the alcohol (100 mg) in pyridine (2 ml). The mixture was kept at room temperature for 4 days and ether (50 ml) was added. The ethereal solution was extracted with hydrochloric acid (3 × 25 ml; 2N) and then washed with solutions of sodium carbonate (3 × 25 ml; 5%) and water (2 × 25 ml).

The alcohol (16) gave the 2-*exo*-toluene-*p*-sulphonate (18) (90%), m.p. 120—121° (from ethanol), τ ($CDCl_3$) 2·22 (2H, m, $|J|_{A,B}$ 8·5 Hz), 2·65 (2H, m, $|J|_{BA}$ 8·5 Hz), 3·2—3·6 (2H, m), 5·2 (1H, q, $|J|_{2,3\text{-}endo}$ 8, $|J|_{2,3\text{-}exo}$ 2·5 Hz), 5·6—5·9 (1H, m), 6·55 (3H, d, $|J|_{H,F}$ 3 Hz), 7·58 (3H, s), 7·7—8·15 (1H, m), and 8·15—8·55 (1H, m).

The alcohol (17) gave the 2-*endo*-toluene-*p*-sulphonate (19) (87%), m.p. 134—135° (from ethanol), τ ($CDCl_3$) 2·28 (2H, m, $|J|_{AB}$ 8·5 Hz), 2·66 (2H, m, $|J|_{BA}$ 8·5 Hz), 3·2—3·6 (2H, m), 5·1 (1H, q, $|J|_{2,3\text{-}exo}$ 9, $|J|_{2,3\text{-}endo}$ 2 Hz), 5·6—5·85 (1H, m), 6·58 (3H, d), $|J|_{HF}$ 3 Hz), 7·58 (3H, s), 7·5—8·0 (1H, m), and 8·3—8·75 (1H, m).

An epimeric mixture of the alcohols (32) and (33) gave a mixture which was separated by preparative layer chromatography. The upper band gave the 2-exo-*toluene*-p-*sulphonate* (34) (42%), m.p. 95° (from ethanol) (Found: C, 56·25; H, 3·6. $C_{20}H_{16}F_4O_4S$ requires C, 56·1; H, 3·8%), τ ($CDCl_3$) 2·26 (2H, m, $|J|_{AB}$ 8·5 Hz), 2·65 (2H, m, $|J|_{BA}$ 8·5 Hz), 3·17 (1H, d, $|J|$ *ca.* 8 Hz), 3·65 (1H, q, $|J|$ *ca.* 8 and 6 Hz), 5·2—5·7 (2H, m), 6·43 (3H, d, $|J|_{H,F}$ 3 Hz), 7·56 (3H, s), 7·78 (1H, q, $|J|$ 13, $|J|_{3\text{-}endo,2}$ 7·5 Hz), and 8·28 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 13, $|J|_{3\text{-}exo,2}$ 2·5 Hz). The lower band gave the 3-endo-*toluene*-p-*sulphonate* (35) (27%), m.p. 91—92° (from methanol) (Found: C, 56·15; H, 3·95%), τ ($CDCl_3$) 2·26 (2H, m, $|J|_{AB}$ 8·5 Hz), 2·65 (2H, m, $|J|_{BA}$ 8·5 Hz), 3·25 (1H, d, $|J|$ *ca.* 8 Hz), 3·7 (1H, q, $|J|$ *ca.* 8 and 6 Hz), 5·0—5·35 (1H, m), 5·45—5·7 (1H, m), 6·43 (3H, d, $|J|_{H,F}$ 3 Hz),

7·74 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 13, $|J|_{3\text{-}exo,2}$ 8 Hz), and 8·38 (1H, q, $|J|_{3\text{-}exo,3\text{-}endo}$ 13, $|J|_{3\text{-}endo,2}$ 3 Hz).

Solvolyses of Toluene-p-*sulphonates*.—(a) The 2-exo-*toluene*-p-*sulphonate* (18). (i) *In trifluoroacetic acid*. The 2-*exo*-tosylate (18) (80 mg) in trifluoroacetic acid (2 ml) was heated under reflux for 2 h. Trifluoroacetic acid was removed under reduced pressure from the cold solution to leave a mixture which was separated by preparative layer chromatography and gave compound (11) (44 mg, 98%), m.p. and mixed m.p. 73° (from hexane) identical (i.r., u.v., and ^{1}H n.m.r. spectra), with the previously prepared compound.

(ii) *In sulphuric acid*. In sulphuric acid (98%) the compound (11) was isolated in 37% yield.

(iii) *In ethanolic hydrochloric acid*. The *exo*-tosylate (18) (50 mg) was heated under reflux in ethanol (5 ml) and hydrochloric acid (5 ml) for 4 h and the mixture was then added to water (10 ml). Extraction with ether and the usual work-up and preparative layer chromatography gave 8-ethoxy-1,2,3,4-tetrafluoro-5,7,8,9-tetrahydro-5,9-methanobenzocyclohepten-6-one (21) (18 mg, 54%), τ (CCl_4) 5·9—6·7 (5H, m), 7·2—8·3 (4H, m), and 8·8 (3H, t, $|J|$ 6·5 Hz), $\nu_{max.}$ 1730 cm^{-1}, M^+ 288.

(b) *The* 2-endo-*toluene*-p-*sulphonate* (19). The *endo*-tosylate (19) (100 mg) was dissolved in acetic acid (6 ml) and acetic anhydride (4 drops) containing sodium acetate (4 mg). The mixture was heated under reflux for 10 min and then at 80° for 12 h, cooled, added to water (50 ml), and extracted with ether (4 × 10 ml). The normal work-up gave compound (8) (52 mg, 92%), m.p. and mixed m.p. 82—83°, identical (u.v., i.r., and ^{1}H n.m.r. spectra) with that obtained previously.

In a second experiment terminated after 6 h two products were obtained: the ketone (8) (67%) and 2-*endo*-acetoxy-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1-methoxy-1,4-ethenonaphthalene (23) (26%), τ ($CDCl_3$) 3·2—3·4 (2H, m), 4·75 (1H, q, $|J|$ 9 and 2·5 Hz), 5·6—5·9 (1H, m), 6·37 (3H, d, $|J|_{H,F}$ 2 Hz), 7·4—7·9 (1H, m), 8·06 (3H, s), and 8·6—9·0 (1H, m), $\nu_{max.}$ 1740 cm^{-1}. Hydrolysis of the acetate (23) with sodium carbonate in aqueous ethanol gave the alcohol (17), identical (t.l.c., i.r., and ^{1}H n.m.r. spectroscopy) with the previously prepared material.

(c) The 2-exo-*toluene*-p-*sulphonate* (34). (i) *In trifluoroacetic acid*. The 2-*exo*-tosylate (34) (100 mg) was dissolved in trifluoroacetic acid (3 ml) and was heated under reflux for 3 h. Removal of the solvent gave a crystalline product which was heated with light petroleum. The insoluble material was toluene-*p*-sulphonic acid; removal of the solvent gave the ketone (5) (52 mg, 92%), m.p. and mixed m.p. 69—72°, identical with previously prepared material (t.l.c., g.l.c., and i.r. and ^{1}H n.m.r. spectroscopy).

(ii) *In sulphuric acid*. The 2-*exo*-tosylate (34) (33 mg) was dissolved in sulphuric acid (1 ml; 98%) at room temperature and poured onto crushed ice (10 g). Conventional work-up gave the ketone (5) (12·2 mg, 72%).

(d) *The* 2-endo-*toluene*-p-*sulphonate* (35). (i) *In trifluoroacetic acid*. The 2-*endo*-tosylate (35) (100 mg) was dissolved in trifluoroacetic acid (3 ml) and heated under reflux for 1·5 h, after which conventional work-up gave 1,2,3,4-tetrafluoro-5,8-dihydro-5-methoxy-9-trifluoroacetoxy-5,8-methanobenzocycloheptene (36) (68 mg, 79%) as an oil, τ ($CDCl_3$) 3·45 (1H, d, $|J|$ *ca.* 6 Hz), 4·04 (2H, m), 6·2—6·8 (4H, m), and 7·2—7·8 (2H, m), $\nu_{max.}$ 1793 cm^{-1}, M^+ 370.

Compound (35) was hydrolysed at room temperature in aqueous ethanolic sodium carbonate and gave the 9-alcohol (37) (100%), $\nu_{max.}$ 3400 cm^{-1}, a solution of which in dichloromethane (1 ml) was added dropwise to a solution of chromium trioxide (90 mg) in pyridine (140 mg) and dichloromethane (2 ml). The solution was stirred for 15 min, chloroform (4 ml) was added, and the mixture was washed successively with sodium hydroxide (5 ml; 1N), hydrochloric acid (5 ml; 1N), and sodium hydrogen carbonate (5 ml; 5%). Removal of the solvent gave a crystalline product (45 mg) which afforded 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5-*methoxy*-5,8-*methanobenzocyclohepten*-9-*one* (38) (31 mg, 73%), m.p. 64—65° (from hexane, then methanol) (Found: C, 57·2; H, 2·9%; M^+, 272. $C_{13}H_8F_4O_2$ requires C, 57·3; H, 2·95%; *M*, 272), τ (CCl_4) 3·43 (1H, d, $|J|$ *ca.* 5·5 Hz), 3·9 (1H, q, $|J|$ *ca.* 5·5 and 3·5 Hz), 6·37—6·75 (1H, m), 6·6 (3H, d, $|J|_{H,F}$ 0·5 Hz), and 7·05—7·55 (2H, m), $\nu_{max.}$ ($CHCl_3$) 1708 cm^{-1}, $\lambda_{max.}$ (EtOH) 249 (ε 4300) and 296 nm (1900).

(ii) *In sulphuric acid*. The 2-*endo*-tosylate (35) (100 mg) was dissolved in sulphuric acid (2 ml; 98%) at room temperature and immediately added to crushed ice (10 g). Extraction with ether and conventional work-up gave the ketone (5) (34 mg, 60%), m.p. and mixed m.p. 70—72°, identical (i.r. and ^{1}H n.m.r. spectra) with authentic material.

Rearrangement of 1,2,3,4-*Tetrafluoro*-5,8-*dihydro*-5-*methoxy*-5,8-*methanobenzocyclohepten*-9-*ol* (37).—Reduction of the ketone (38) with lithium aluminium hydride gave an epimeric mixture of the alcohols (37) in 87% yield. This material (8·7 mg) was dissolved in sulphuric acid (0·2 ml; 98%) and added to ice (1 g). Conventional work-up gave the ketone (5) (6·7 mg, 87%), m.p. 68—71°, identical with authentic material (t.l.c., g.l.c., and i.r. spectroscopy).

Attempted Equilibration Reactions with the Ketones (4), (5), (8), *and* (11).—(i) *In trifluoroacetic acid*. The ketones (5), (8), and (11) were heated under reflux in trifluoroacetic acid in separate experiments and were recovered completely unchanged after 675, 110, and 100 h, respectively.

(ii) *In sulphuric acid*. The ketones (5), (8), and (11) were dissolved in sulphuric acid (98%) at room temperature and were recovered unchanged after 3, 1, and 3 h, respectively. Similarly the ketone (4) was recovered unchanged after 2 min at room temperature.

(iii) *In sulphuric acid over an extended period*. The ketone (8) was dissolved in sulphuric acid (98%) and the solution worked up after 209 h. The mixture obtained was shown not to contain either of the ketones (5) and (11) by i.r. and ^{1}H n.m.r. spectroscopy and by t.l.c. and g.l.c.

Similarly the ketone (5) gave, after 22 h, starting material (11%) and the ketone (11) (23%), together with other material which was shown not to be the ketone (8).

Similarly the ketone (11) gave, after 192 h, starting material (97% recovery).

Attempted Equilibration Reactions of the Ketones (13) *and* (14).—When the ketones (13) and (14) in separate experiments were heated under reflux in trifluoroacetic acid for 18 h, or kept at room temperature in sulphuric acid (98%) for 24 h or at room temperature in fluorosulphonic acid for 20 h, no isomerisation to the other ketone was detected by g.l.c., t.l.c., or i.r. spectroscopy.

Deuteriation Experiments. Rearrangement of Compound (2) *in Deuteriosulphuric Acid*.—Compound (2) was dissolved in deuteriosulphuric acid and deuterium oxide (4 : 1) and, after the usual work-up, gave 5,6,7,8-tetrafluoro-3,4-dihydro-1,4-etheno[3-^{2}H]naphthalen-2(1*H*)-one (26) (60%), τ (CCl_4) 3·0—3·5 (2H, m), 5·2—5·5 (2H, m), 7·8—8·0 (0·41H,

m), and 8·0—8·2 (0·59H, m), M^{+} 243. Photolysis of the ketone (26) gave 1,2,3,4-tetrafluoronaphthalene, M^{+} 200 (^{2}H 0%). In addition, 1,2,3,4-tetrafluoro-5,9-dihydro-[7,10-$^2H_2$]-5,9-methanobenzocyclohepten-6-one (27) (4%) was isolated; τ (CCl_4) 2·62 (1H, d, $|J|$ *ca.* 7 Hz), 5·8—6·05 (2H, m), and 7·1—7·4 (1H, m), M^{+} 244 ($^2H_2$ 94%, ^{2}H 6%).

The ketone (11) was similarly dissolved in deuteriosulphuric acid–deuterium oxide and after 10 min at 60° the usual work-up gave 1,2,3,4-tetrafluoro-5,9-dihydro[7-^{2}H]-5,9-methanobenzocyclohepten-6-one (90%), τ (CCl_4) 2·63 (1H, d, $|J|$ *ca.* 7 Hz), 5·8—6·15 (2H, m), and 7·1—7·3 (2H, m), M^{+} 243 (^{2}H 93%).

Preparation of Deuteriated Anisoles and Deuteriated 5,6,7,8-Tetrafluoro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalenes.—(i) [2,4,6-$^2H_3$]*Anisole.* 2,4,6-Tribromophenol was converted [23] into 2,4,6-tribromoanisole (97%) in dimethylsulphoxide and into 4-bromo[2,6-$^2H_2$]anisole (69%) [17] and hence [18] into [2,4,6-$^2H_3$]anisole (65%), τ (CCl_4) 2·84br (2H, s) and 6·27 (3H, s), M^{+} 111 ($^2H_3$ 99%).

(ii) [4-^{2}H]*Anisole. p*-Bromophenylmagnesium bromide was prepared in ether and deuteriolysed with deuterium oxide in tetrahydrofuran to afford [4-^{2}H]anisole (75%), τ (CCl_4) 2·78 (2H, m, $|J|_{AB}$ 9 Hz) and 3·18 (2H, m, $|J|_{BA}$ 9 Hz), M^{+} 109 (^{2}H 87%).

(iii) [3,5-$^2H_2$]*Anisole.* 1,3,5-Tribromobenzene was converted [17] (42%) into 1,3-dibromo[5-^{2}H]benzene, and hence [21] into 1-bromo[3,5-$^2H_2$]benzene in 67% yield. The 1-bromo-[3,5-$^2H_2$]benzene was converted into [3,5-$^2H_2$]phenol in 49% yield (*via* the Grignard reagent and dimethyl [3,5-$^2H_2$]-phenyl borate [22]), which was converted [23] into [3,5-$^2H_2$]-anisole in 86% yield, M^{+} 110 ($^2H_2$ 77%, ^{2}H 19%).

The deuteriated anisoles were converted [9] into the deuteriated 1-methoxy-1,4-ethenonaphthalenes by using pentafluorophenylmagnesium bromide as the source of tetrafluorobenzyne. [2,4,6-$^2H_3$]Anisole gave 5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy[2,4,10-$^2H_3$]-1,4-ethenonaphthalene (39), τ (CCl_4) 3·2br (2H, s) and 6·3 (3H, d, $|J|_{H,F}$ 3 Hz), M^{+} 259 ($^2H_3$ 99%).

[4-^{2}H]Anisole gave 5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy[4-^{2}H]-1,4-ethenonaphthalene (41), τ (CCl_4) 3·0 (2H, d, $|J|_{AB}$ 7 Hz), 3·23 (2H, d, $|J|_{BA}$ 7 Hz), and 6·29 (3H, d, $|J|_{H,F}$ 3 Hz), M^{+} 257 (^{2}H 89%).

[3,5-$^2H_2$]Anisole gave 5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy[3,9-$^2H_2$]-1,4-ethenonaphthalene (40), τ (CCl_4) 2·9—3·1 (2H, m), 4·7—5·0 (1H, m), and 6·3 (3H, d, $|J|_{H,F}$ 3 Hz), M^{+} 258 ($^2H_2$ 76%, ^{2}H 18%).

Rearrangements of the Deuteriated Compounds (39)—(41).—Reactions were carried out in 98% sulphuric acid and in the case of the compound (39) in 80% sulphuric acid. The compounds corresponding to (5), (8), and (11) were isolated and analysed by ^{1}H n.m.r. and mass spectrometry. In the case of the compounds corresponding to (5) these were photolysed and the deuteriated 1,2,3,4-tetrafluoronaphthalenes produced were analysed by ^{1}H n.m.r. and mass spectrometry. The data obtained are collected in Tables 1—4.

Reaction of 5,6,7,8-*Tetrafluoro*-3,4-*dihydro*[9-^{2}H]-1,4-*ethenonaphthalen*-2(1H)-*one* (29) *in Sulphuric Acid.*—The ketone (29) (9-^{2}H 87%) (obtained from the reaction of tetrafluorobenzyne with [4-^{2}H]anisole) (300 mg) was dissolved in sulphuric acid (4 ml) and after 192 h was added to crushed ice (20 g) and worked up by the usual method. Preparative layer chromatography gave unchanged starting material (upper band) (29 mg, 10%), as indicated by ^{1}H n.m.r. spectroscopy and mass spectrometry, and 1,2,3,4-tetrafluoro-5,9-dihydro[9-^{2}H]-5,9-methanobenzocyclohepten-6-one (30) (lower band) (67 mg, 22%), τ (CCl_4) 2·6 (1H, d, $|J|$ 10 Hz), 4·52 (1H, q, $|J|$ 10 and 1·5 Hz), 5·8—6·05 (1H, m), and 7·1—7·3 (2H, m), M^{+} 243 (^{2}H 87%).

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