Oxidation of Some Aromatic Hydrocarbons by Cerium(IV) Trifluoroacetate

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The preparation of cerium(IV) trifluoroacetate, and its reactions with some benzenoid hydrocarbons in trifluoroacetic acid containing lithium trifluoroacetate, are described. With electron-rich compounds, oxidation is rapid at room temperature; the products are biaryls, diarylmethanes, and trifluoroacetate esters, the proportions of which depend on the structure of the aromatic compound. Evidence is presented that the first step is the transfer of one electron to the oxidant to form an aromatic radical cation; with methyl-substituted benzenes, this is followed either by reaction with another aromatic molecule or by deprotonation, subsequent reactions then yielding an ester or a diarylmethane.

WE have reported previously that methyl-substituted benzenes are oxidised readily at low temperatures by lead tetra-acetate in trifluoroacetic acid to give mainly biaryls and diarylmethanes, the relative amounts of which vary widely with the structure of the aromatic compound.[1,2] Evidence was obtained that the first step is the removal of one electron from the aromatic compound and that the resulting radical cation can either react with another aromatic molecule to produce a biaryl or yield a benzylic cation which leads to diarylmethanes.[1]

One of the problems in elucidating the mechanisms of reactions involving lead(IV) is that the oxidant can bring about both one- and two-electron oxidations. For example, as well as the one-electron processes described above, lead(IV) can effect electrophilic plumbylation of an aromatic ring and the resulting aryl-lead compound can decompose by cleavage of the C-Pb bond with loss of lead(II). To obviate this difficulty an oxidant is required which is capable solely of one-electron oxidation. Manganese(III) and cobalt(III) acetates in acetic acid have been employed, but reaction is generally sluggish, high temperatures are necessary, and, for example, radicals derived from the solvent complicate the issue.[3] Cerium-(IV) compounds are potentially suitable, but of the commonest, the sulphate is not soluble in inert organic solvents and the ammonium nitrate can lead to complex mixtures of products.[4] However, we have found that cerium(IV) trifluoroacetate can be prepared readily and its use avoids these difficulties.

The reaction of cerium(IV) hydroxide with trifluoroacetic acid gave the basic salt $Ce(OH)_2(O_2C\cdot CF_3)_2$ which, on further treatment with the acid and its anhydride, yielded cerium(IV) trifluoroacetate. Its analytical figures agreed satisfactorily with the formula $Ce(O_2C\cdot CF_3)_4$ after intensive drying, but in this form it tended to undergo hydrolysis in air (cf. the behaviour of lead tetracarboxylates). For this reason it was usually found more satisfactory to use less thoroughly dried material. The compound is a powdery solid which is insoluble in chloroform, dichloromethane, and benzene, but soluble in many potentially co-ordinating solvents (e.g. acetone, 1,2-dimethoxyethane, dimethyl sulphoxide, and acetonitrile) which, however, undergo oxidation with varying degrees of ease. It is not significantly soluble in trifluoroacetic acid alone but can be dissolved to give up to a ca. 0·1M-solution when lithium, sodium, or potassium trifluoroacetate is also present; presumably the cerium ion is present as an anionic complex under these conditions. These solutions are stable, at least in the absence of light, and because use of the lithium salt allows larger quantities of the aromatic compound to be dissolved, we employed this salt for oxidations. The standard procedure was to dissolve cerium(IV) trifluoroacetate in a refluxing solution of 1·33M-lithium trifluoroacetate in trifluoroacetic acid and add a small amount of trifluoroacetic anhydride to the cooled solution to remove adventitious water. This solution was introduced drop-

[1] R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J.C.S. Perkin I*, 1973, 325.

[2] R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc. (B)*, 1971, 518.

[3] E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 138; P. J. Andrulis, jun., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *ibid.*, 1966, **88**, 5473.

[4] L. A. Dust and E. W. Gill, *J. Chem. Soc. (C)*, 1970, 1630; B. Rindone and C. Scolastico, *J. Chem. Soc. (B)*, 1971, 2238.

wise into a stirred solution of the benzenoid compound in trifluoroacetic acid containing lithium trifluoroacetate and a little of the acid anhydride at 25°; the benzenoid compound was used in large excess in an attempt to minimise the importance of oxidation of the products. Work-up conditions were established under which any trifluoroacetate-ester products were not appreciably hydrolysed.

The oxidation of mesitylene occurred essentially instantaneously and gave bimesityl (1), the diarylmethane (2), and the benzylic trifluoroacetate (3). Their yields varied with the concentration of mesitylene as shown in Table 1. The dependences of the yields on the concentration of lithium trifluoroacetate and the temperature are in Table 2 (the yield of the benzylic ester was never more than 1% under these conditions and is omitted).

(1) (2)

(3)
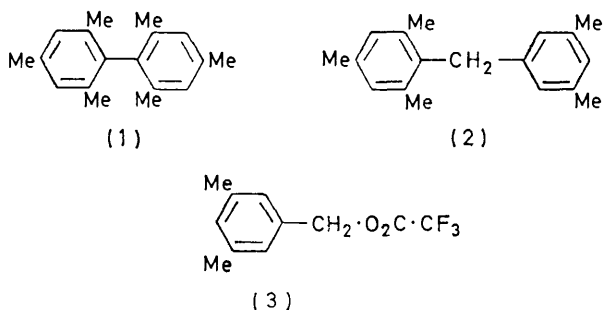
Benzene was not oxidised under these conditions at a significant rate. When reaction was carried out at

TABLE 1

Products from the oxidation of mesitylene

	Amount of	Products (mol %)		
Expt.	mesitylene (ml) *	(1)	(2)	(3)
1	1	27	9	4
2	3	40	11	<1
3	7	38	10	<1

* In 20 ml of reactant solution.

TABLE 2

Dependence of the products from mesitylene on [CF$_3$·CO$_2$Li] and temperature

		Temp.	Products (mol %)		
Expt.	[CF$_3$CO$_2$·Li](M)	(°C)	(1)	(2)	Ratio
4	0—0·4 *	25	55	3	18
5	0·4	25	42	7	6
6	0·4	100	25	23	1·1
7	1·33	100	11	34	0·3

* Lithium trifluoroacetate (0·4M) was included only in the oxidant solution.

reflux temperature (ca. 70°), the cerium(IV) ion was consumed within 24 h, phenyl trifluoroacetate (8%) and biphenyl (1%) being formed; a control experiment showed that, had biphenyl been formed in significant yield, most of it would have been lost through further oxidation. Toluene did not react as readily as mesitylene, but oxidation was complete within a few minutes at 25°; o- and p-phenyltolylmethane and benzyl trifluoroacetate were produced but no bitolyls were detected. (A check

experiment showed that 4,4'-bitolyl in a large excess of toluene was itself oxidised but that it was never completely destroyed: we assume therefore that bitolyls are not formed from toluene.) p-Xylene and durene reacted essentially instantaneously at 25°; the former gave the diarylmethane (4) and p-methylbenzyl trifluoroacetate but no bixylyl, and the latter gave the diarylmethane (5) and biduryl but no trifluoroacetate ester. The yields of the products from methylbenzenes given in Table 3 were

TABLE 3

Products from four methyl-substituted benzenes

		Products (mol %)	
Reactant	Biaryl	Diarylmethane	Ester
Toluene		15 *	15
p-Xylene		37	8
Mesitylene	38	10	<1
Durene	2	97	

* Mixture of o- and p-phenyltolylmethane.

obtained under identical conditions except that the concentration of durene was only about one-half that of the other aromatic compounds because of its low solubility in trifluoroacetic acid.

(4) (5)

(6) (7)

(8)
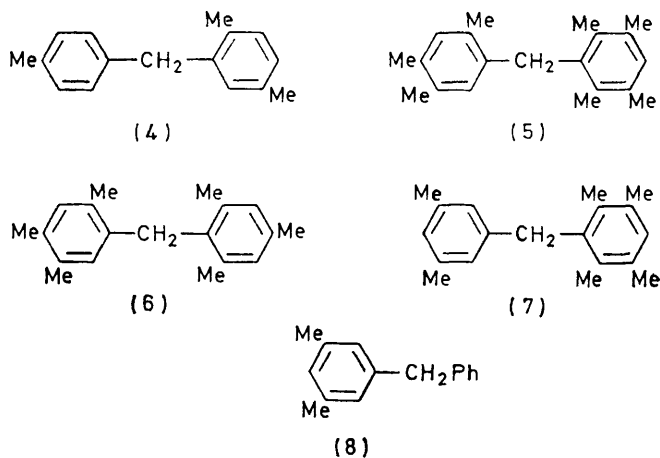
The oxidation of an equimolar mixture of mesitylene and durene gave mainly (84%) the diarylmethane (6), together with small quantities of the compounds (2), (5),* and (7) (8, 3, and 2%, respectively). That of a mixture of mesitylene and a 50-fold excess of benzene gave 37% of the diarylmethane (8) and 3% of (2). Anisole yielded 2,2'-, 2,4'-, and 4,4'-dimethoxybiphenyl (1, 2, and 27%, respectively).

Mechanistic Features and Comparison with Lead(IV).— The results can be accounted for by the paths outlined in the Scheme; individual aspects are discussed later.

The following observations are consistent with initial formation of the aromatic radical cation. First, biaryls are formed from benzene, anisole, mesitylene, and durene, in accord with reaction (i). Secondly, the ease of reaction increases in the order, benzene < toluene < p-xylene, which is the order of decreasing ionising potential (cf. ref. 1); further, the products from a mixture of

* Compound (5) was shown not to react further to any appreciable extent in trifluoroacetic acid.

mesitylene and durene show that the former is converted less efficiently than the latter into an active entity for aromatic substitutions, in accord with the lower ionisation potential of durene and rate-determining electron transfer. Thirdly, under the same conditions the ratio of the yields of biaryl and diarylmethane is much greater than unity for mesitylene but negligible for durene, just as it is in anodic oxidation, in which the first step is electron transfer.[5]

The suggested competition for the first-formed radical cation between reaction with aromatic compound and deprotonation is supported by the results in Tables 1 and 2. Thus, there is a small but significant increase in

allowance for the excess of benzene in the latter experiment) it is also more reactive than benzene towards the benzylating agent from mesitylene. The relative reactivities which are implied are those for aromatic electrophilic substitutions; the selectivity is relatively small, just as it is in some Friedel–Crafts benzylations.[7]

The pattern of products is broadly similar to that obtained with lead(IV) in trifluoroacetic acid and lends support to the interpretation [1,2] of those oxidations. Thus, with both oxidants, p-xylene and durene give almost entirely the corresponding diarylmethanes, an equimolar mixture of mesitylene and durene gives the 'crossed' diarylmethane (6) as major product, and

SCHEME
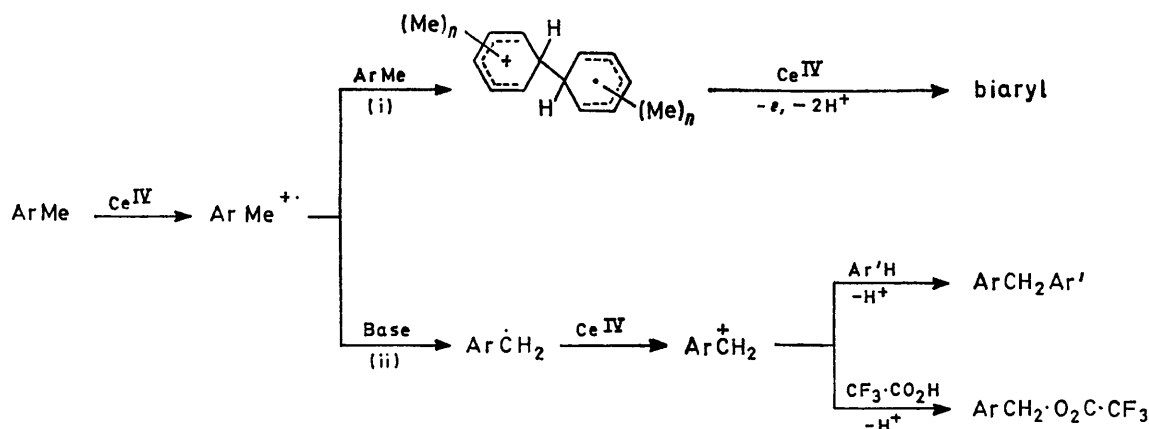
the yield of biaryl (1) compared with that of diarylmethane (2) when the concentration of mesitylene is increased, and a marked decrease in this ratio when the concentration of lithium trifluoroacetate (which should act as a base under these conditions) is increased (compare experiment 4 with 5 and 6 with 7). The effect of raising the temperature suggests that the reaction with base has the higher activation energy (compare experiment 5 with 6).

Any arylmethyl radicals arising from the initial radical cations by deprotonation would be expected readily to undergo one-electron oxidation with cerium(IV),[6] so that the absence of 1,2-diarylethanes is unexceptional. That the diarylmethanes are formed from arylmethyl cations by electrophilic substitution is in accord with two observations. First, the relative yields of diarylmethanes and benzylic trifluoroacetates increase in the order, toluene < p-xylene < mesitylene, durene, consistent with competition for the benzylic cation between trifluoroacetate anion (or the acid) and increasingly strongly nucleophilic aromatic carbon. Secondly, the relative yields of the diarylmethanes (6) and (5) and of (2) and (7), from a mixture of mesitylene and durene, and of (2) and (8), from a mixture of mesitylene and benzene, show that mesitylene is more reactive than durene towards the benzylating entity from either species and that (making

mesitylene gives mainly bimesityl [providing that, with cerium(IV), the temperature is low]. The behaviour of toluene is different, for with lead(IV) the yield of bitolyls is much greater than that of diarylmethanes.[2] In part, this will be the result of the presence of lithium trifluoroacetate in the cerium(IV) oxidation and the consequent facilitation of reaction (ii); however, the possibility cannot be discounted that cerium(IV) trifluoroacetate can abstract a hydrogen atom from a methyl group, as well as an electron from an aromatic ring, and that this reaction is the preferred one when the ionisation potential of the aromatic ring is relatively high, as with toluene.

EXPERIMENTAL

Cerium(IV) *Trifluoroacetate.*—During this preparation, precautions to exclude water and light were taken whenever appropriate. 2M-Sodium hydroxide (50 ml) was added to a solution of cerium(IV) sulphate (3·98 g, 10 mmol) in M-sulphuric acid (25 ml) and water (25 ml) to precipitate cerium(IV) hydroxide. This was filtered off, washed with distilled water several times, and sucked dry at the pump, but not desiccated, and then heated in trifluoroacetic acid until dissolution was complete. Evaporation of the solvent left a yellow, powdery solid of composition $Ce(OH)_2$-$(O_2C\cdot CF_3)_2,H_2O$ which, after being heated at 100° under water-pump vacuum, yielded a solid of composition $Ce(OH)_2(O_2C\cdot CF_3)_2$. This salt gave a deep yellow solution in a mixture of trifluoroacetic anhydride (5 ml) and tri-

[5] K. Nyberg, *Acta Chem. Scand.*, 1970, **24**, 1609.

[6] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1971, **93**, 995.

[7] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

fluoroacetic acid (10 ml); after being heated under reflux for 2 h, a yellow solid was deposited and the supernatant liquid was colourless. The solid had M, typically, in the range 610—660 on titration for Ce(IV) [Ce($O_2C \cdot CF_3$)$_4$ requires 592] and, after being heated at 110° under water-pump vacuum in the presence of silica gel, M 592 $\pm$ 3.

Cerium(IV) was determined by dissolving the solid in excess of dilute sulphuric acid, adding to excess of iron(II) ammonium sulphate solution, and estimating the remaining iron(II) with potassium permanganate [standardised against the iron(II) solution]. Trifluoroacetate was determined by hydrolysis of the solid by boiling with three successive portions of dilute sodium hydroxide solution, filtering off the residual solid through sintered glass, and estimating the excess of sodium hydroxide with hydrochloric acid.

Lithium trifluoroacetate was obtained by adding lithium carbonate to a slight excess of trifluoroacetic acid in water (1 : 1), warming until the evolution of carbon dioxide ceased, and evaporating to dryness followed by desiccation at 110°.

Methods.—^{1}H N.m.r. and mass spectrometry and g.l.c. were performed as described previously; [1] g.l.c. was carried out on 10% silicone oil (MS 550) or Apiezon L coated on Celite.

Except for variations noted in the text, the procedure for oxidations was as follows. Cerium(IV) trifluoroacetate (0·5 mmol) was dissolved in a 1·33M-solution of anhydrous lithium trifluoroacetate in trifluoroacetic acid (10 ml) by heating at the reflux temperature for *ca.* 15 min. The yellow solution was allowed to cool, treated with trifluoro-acetic anhydride (1 ml), and left for 5 min. It was added dropwise to a stirred solution of the aromatic compound (7 ml) in trifluoroacetic acid (12 ml) containing 0·4M-lithium trifluoroacetate and trifluoroacetic anhydride (1 ml) at 25°.

Mixtures after oxidation were poured into light petroleum (b.p. 60—80°; 40 ml) containing an internal standard for g.l.c. Water was added, and the petroleum layer and two further petroleum extracts were combined, dried ($MgSO_4$), and (except for products from benzene or toluene, the trifluoroacetate esters from which are fairly volatile) evaporated. The residue was submitted to g.l.c.–mass spectrometry; products were identified both by their g.l.c. retention times and by their mass spectra, and the chromatograph was calibrated for quantitative analysis with authentic samples.

3,5-Dimethylbenzyl trifluoroacetate, isolated by preparative g.l.c. following a large scale oxidation of mesitylene, showed τ 2·66 (1H, s, 4-H), 3·12 (2H, s, 2-H), 4·75 (2H, s, CH_2), and 7·70 (6H, s, CH_3): m/e 232 (M^+, 45%), 135 ($M - CF_3CO$, 19), 119 ($M - CF_3CO_2$, 100), 118 ($M - CF_3CO_2H$, 28), 117 (29), 107 (18), 105 (11), 104 (10), 103 (15), 91 (36), and 69 (13); m^* 78·5 (232 $\longrightarrow$ 135) and 60·0 (232 $\longrightarrow$ 118). Other products were available from previous studies [1,2] except for 3,5-dimethylphenyl-(2,3,5,6-tetramethylphenyl)methane which was identified from its mass spectrum following g.l.c.