

Reactions of Lead(IV). Part XXVII.¹ Oxidative Rearrangement of Styrene and Related Compounds to Aldehydes or Ketones in the Presence of Trifluoroacetic Acid

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Aryl-conjugated olefins can undergo oxidative rearrangement to carbonyl compounds when treated with lead tetra-acetate in trifluoroacetic acid at room temperature. Excellent yields of arylacetaldehydes are obtained from styrene and some ring-substituted derivatives, but there are limitations to the synthetic utility of the method for other aryl-conjugated olefins.

THE oxidation of olefins by lead tetra-acetate generally gives a complex mixture of products, and it is comparatively rare for one to be formed in synthetically useful yield. Reactions of both heterolytic and homolytic type are involved, depending upon the structure of the olefin and the reaction conditions; thus, the former type of reaction can lead to *vic*-hydroxy-acetates and diacetates, and enolic and allylic acetates, and the latter to the addition of a methyl and an acetoxy-group across the double bond.²⁻⁴

¹ Part XXVI, R. O. C. Norman, R. Purchase, and C. B. Thomas, *J.C.S. Perkin I*, 1972, 1701.

² R. Criegee, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Part A, Academic Press, 1965, ch. 5.

³ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 771.

In a limited number of cases, products resulting from skeletal rearrangement have been obtained. One process of this type involves the nucleophilic rearrangement of an aryl group within an oxyplumbylation adduct (2) formed from an olefin (1); this yields a carbonyl compound or a derivative such as the 1,1-diacetate.³⁻⁶ The yield of rearranged product is likely to depend, first, on the ease of formation of the oxyplumbylation adduct as compared with alternative reactions such as a homolytic process and, secondly, on the migratory aptitude of the aryl group, since an alternative reaction of the

⁴ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1968, 994.

⁵ R. Criegee, P. Dimroth, K. Noll, R. Simon, and C. Weis, *Chem. Ber.*, 1957, **90**, 1070.

⁶ H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

adduct (2) is formation of the cyclic acetoxonium ion (4) and thence hydroxy-acetates and derived products. For example, we can rationalise in this way the observations that, whereas *p*-methoxystyrene gives *p*-methoxyphenylacetaldehyde 1,1-diacetate in 90% yield when treated with lead tetra-acetate in acetic acid at room temperature,⁵ the oxidation of styrene in this solvent requires more vigorous conditions and gives phenylacetaldehyde or its derivatives in much lower yield,^{3,6} for the *p*-OMe group should assist both the electrophilic oxyplumbylation and the aryl migration. There is evidence, too, that the oxyplumbylation adducts from *cis*- and *trans*- β -methylstyrene, unlike those from styrene or α -methylstyrene, undergo acetoxonium-ion formation in preference to aryl migration, and an explanation for this has been suggested.⁴

It follows that, in order to obtain good yields of the oxidative rearrangement product under mild conditions, it is desirable to use a lead(IV) derivative which is a more reactive electrophile than the tetra-acetate and the ligands of which provide, as β -substituents, less effective

the yield of phenylacetaldehyde from styrene is far higher than that of its derivatives under the conditions used previously,^{3,6} and β -methylstyrene gives a moderate

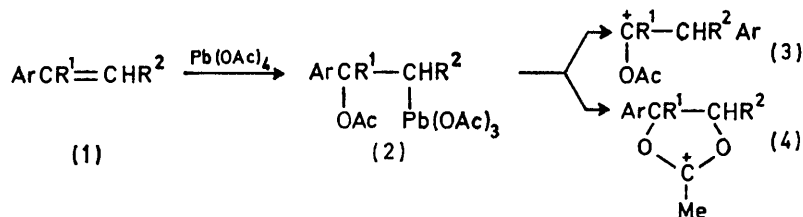
TABLE 1

Carbonyl compounds formed by oxidative rearrangement of olefins with lead(IV) in the presence of trifluoroacetic acid

Olefin	Carbonyl compound	Yield (%)
PhCH ₂ :CH ₂	PhCH ₂ :CHO	98
<i>p</i> -ClC ₆ H ₄ :CH:CH ₂	<i>p</i> -ClC ₆ H ₄ :CH ₂ :CHO	90
<i>p</i> -O ₂ N:C ₆ H ₄ :CH:CH ₂	<i>p</i> -O ₂ N:C ₆ H ₄ :CH ₂ :CHO	98
<i>p</i> -MeC ₆ H ₄ :CH:CH ₂	<i>p</i> -MeC ₆ H ₄ :CH ₂ :CHO	86
PhCMe:CH ₂	PhCH ₂ :COMe	55
<i>p</i> -O ₂ N:C ₆ H ₄ :CMe:CH ₂	<i>p</i> -O ₂ N:C ₆ H ₄ :CH ₂ :COMe	91
<i>p</i> -MeC ₆ H ₄ :CMe:CH ₂	<i>p</i> -MeC ₆ H ₄ :CH ₂ :COMe	18
PhCH:CHMe ^a	PhCHMe:CHO	55
Ph ₂ C:CH ₂	PhCH ₂ :COPh	32
PhCH:CHPh ^a	Ph ₂ CH:CHO	5

^a *trans*.

yield of aldehyde whereas none was obtained with acetic acid as solvent; this is in accord with the view that, whereas phenyl migration occurs less readily than



SCHEME 1

participating groups than acetate. Lead tetrakis(trifluoroacetate)⁷ appears to be such a species; it is a more powerful oxidant than the tetra-acetate,⁷ and we should not expect a β -trifluoroacetoxy-substituent to have significant neighbouring-group activity. We have found that a solution of lead tetra-acetate in trifluoroacetic acid is likewise a powerful oxidant,⁸ doubtless because it contains lead(IV) with up to four trifluoroacetate ligands, and since this system obviates the need to prepare the tetrakis(trifluoroacetate), we chose it for the oxidation of a number of aryl-conjugated olefins.

With certain limitations, these expectations were realised in practice. The carbonyl compounds formed by oxidative rearrangement are recorded in Table 1; they were obtained by the slow addition of a solution of the olefin in dichloromethane to one of lead tetra-acetate in trifluoroacetic acid at room temperature, with a total reaction time of 1 h (the olefin was not dissolved in the acid in order to reduce the chance of proton-initiated reactions; see later). Only traces of the carbonyl compounds from 2- or 4-vinylpyridine were obtained, even after several hours at 60°, and no carbonyl compounds were obtained from benzylideneacetone or 4,4'-dinitro-*trans*-stilbene.

We draw attention to the following features. First,

⁷ R. E. Partch, *J. Amer. Chem. Soc.*, 1967, **89**, 3662.

⁸ R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc. (B)*, 1971, 518.

formation of the cyclic acetoxonium ion in the latter case, it occurs in preference to participation by a β -trifluoroacetoxy-group. Second, the formation of *p*-nitrobenzyl methyl ketone in 91% yield from α -methyl-*p*-nitrostyrene shows that even the *p*-nitrophenyl group, which has a relatively weak migratory aptitude, migrates efficiently; we presume that it is also the *p*-nitrophenyl group, and not hydrogen, which migrates in the oxidation of *p*-nitrostyrene.

Third, it is notable that the yield of the rearrangement product from an α -methylstyrene increases in the order *p*-Me < *p*-H < *p*-NO₂, the opposite of that expected on the basis of migratory aptitudes. To investigate this further, we examined the reaction of α -methylstyrene for by-products, obtaining 39% of the dimer (5) and 1 and 2%, respectively, of *o*- and *p*-chlorobenzyl methyl ketone. The chloro-derivatives no doubt owe their origin to chloride impurities in the lead(IV) which are not removed by normal purification procedures;⁹ such products have been noted before.⁹ The dimer (5) presumably arises *via* protonation of α -methylstyrene as in Scheme 2;¹⁰ dimerisation of this type, and linear polymerisation, should be facilitated by electron-releasing groups, and competition of processes of this

⁹ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1970, 421.

¹⁰ J. C. Petropoulos and J. J. Fisher, *J. Amer. Chem. Soc.*, 1958, **80**, 1938; J. M. Barton and D. C. Pepper, *J. Chem. Soc.*, 1964, 1573.

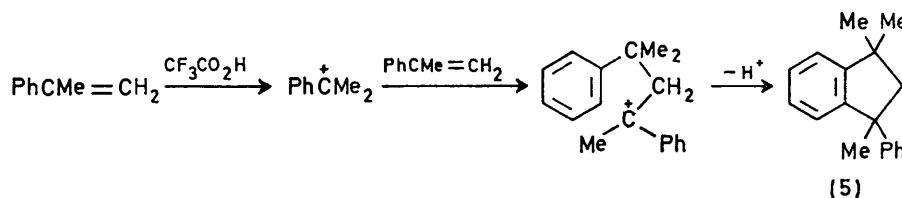
type with oxidative rearrangement may account for the trend in yields from the latter process referred to above.

Reduction in the acidity of the medium should decrease the ease of protonation and might thereby result in more efficient oxidative rearrangement. We therefore studied the oxidation of α -methylstyrene in various mixtures of trifluoroacetic acid and acetic acid, as well as in each separately; the temperature was increased to 60° for these comparative experiments since reaction at room temperature was very slow in mixtures containing mainly acetic acid. The results are in Table 2; in

such as amino). With other aryl-conjugated olefins, the method is likely to be useful only if the aryl group is not too strongly electron-withdrawing (*e.g.* protonated pyridyl) and the olefin is not especially reactive in proton-catalysed processes.

EXPERIMENTAL

¹H N.m.r. spectra were measured for solutions in deuteriochloroform on a Perkin-Elmer R10 60 MHz spectrometer. Mass spectra were determined on an A.E.I. MS12 spectrometer which could be coupled *via* a heated capillary to a



SCHEME 2

addition to the dimer (5) and benzyl methyl ketone, PhCH(OAc)·COMe (6),⁴ PhC(CH₂·OAc)·CH₂ (7),⁴ and PhCMe(OAc)·CH₂Cl (8) were formed in small yields, as

TABLE 2

Products from the oxidation of α -methylstyrene in mixtures of acetic acid and trifluoroacetic acid at 60°

[CF ₃ ·CO ₂ H] : [HOAc]	Products (%)				
	PhCMe·-CH ₂	(5)	PhCH ₂ ·-COMe (6)	(7)	(8)
1 : 0	2	49	33		
1 : 0·3	3	24	40	2	
1 : 1	1	Trace	54	7	
1 : 3	1		56	3	Trace 2
0 : 1			40	5	4

well as traces of the chlorobenzyl methyl ketones (first three experiments) and, in acetic acid alone, benzyl methyl ketone diacetate (20%) and PhCMe(OH)·CH₂·OAc (18%). Thus, the efficiency of dimer formation does indeed fall off as the acidity of the medium is decreased. However, the decrease in the yield of dimer is only partly offset by an increase in the yield of benzyl methyl ketone, the maximum yield of which (including its diacetate) is 60%.

In summary, lead tetra-acetate in trifluoroacetic acid is an excellent reagent for the synthesis of arylacetaldehydes from styrene and some of its ring-substituted derivatives; the substituents can be either electron-withdrawing or (weakly) electron-releasing. The method complements the use of this oxidant in acetic acid which is successful when the substituent is the strongly electron-releasing *p*-OMe group, for which also thallium(III) nitrate in methanol is an excellent reagent,¹¹ and is more suitable than those in which higher temperatures are necessary, because of the tendency of the products to polymerise on heating (however, it would not be suitable when the substituent is a readily oxidisable one,

gas chromatograph. M.p.s were measured on a Kofler micro hot-stage. Gas chromatography was performed on a Pye instrument (series 104, model 24) with 5 ft columns packed with polyethylene glycol adipate (PEGA), Carbowax 20M, Apiezon-L, or silicone oil (MS 550), each as a 10% coating on Celite.

Materials.—Lead tetra-acetate (B.D.H. laboratory reagent) was sucked dry at the pump; no attempt was made to remove residual acetic acid since hydrolysis is then rapid, and iodometric titration showed that the solid contained 90% of lead tetra-acetate, allowance being made for 10% acetic acid when the material was weighed. Dichloromethane was heated under reflux over P₂O₅ for 24 h and distilled before use. Trifluoroacetic acid was the commercial material, as were all the olefins except the following two.

p-Nitrostyrene was prepared by distilling in steam a mixture of *p*-nitrophenethyl bromide (5 g), triethanolamine (30 ml), and water (15 ml) (*cf.* ref. 12) and was obtained as pale yellow crystals, m.p. 20·5—21·5° (from light petroleum at 0°) (*lit.*,¹² 21·4°). α -Methyl-*p*-nitrostyrene was prepared from *p*-nitrocumene¹³ by radical-catalysed bromination followed by dehydrobromination¹⁴ and had m.p. 50—52° (from light petroleum) (*lit.*,¹⁴ 51—54°); τ 1·87 and 2·45 (4H, *ca.* AB quartet, *J* 8·8 Hz), 4·51 (1H, m), 4·75 (1H, m), and 7·82 (3H, m).

Oxidations.—The following procedure was typical. Styrene (0·01 mol) in dichloromethane (20 ml) was added dropwise during 30 min to a well-stirred solution of lead tetra-acetate (0·01 mol) in trifluoroacetic acid (10 ml) at room temperature. Reaction was complete within a few min of the addition and, after being stirred for a further 30 min, the mixture was poured into water and the ether extract was washed (NaHCO₃ and water) and dried (MgSO₄). Evaporation of the solvent left a faintly yellow oil of which part was submitted to g.l.c. followed by mass spectrometry and part was analysed by n.m.r. Phenylacetaldehyde was identified by both techniques and its yield was estimated by g.l.c.

¹¹ A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Letters*, 1970, 5275.

¹² R. W. Strassburg, R. A. Gregg, and C. Walling, *J. Amer. Chem. Soc.*, 1947, **69**, 2141.

¹³ R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1939, 1299.

¹⁴ G. Brubacher and E. Suter, *Helv. Chim. Acta*, 1950, **33**, 256.

When the compound was a solid, further confirmation of its structure was obtained from the m.p. of the recrystallised material. For example, *p*-nitrostyrene gave *p*-nitrophenylacetaldehyde as almost colourless crystals, m.p. 83—85° (from light petroleum) (lit.,¹⁵ 85—86°); τ 0.10 (1H, t, *J* 1.7 Hz), 1.71 and 2.53 (4H, *ca.* AB quartet, *J* 8.9 Hz), and 6.10 (2H, d, *J* 1.7 Hz).

From the reaction of α -methylstyrene, 1,1,3-trimethyl-3-phenylindane (5) was isolated by chromatography on

¹⁵ 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

alumina with benzene and obtained as a white solid, m.p. 50—52° (from methanol) (lit.,¹⁶ 50—52°); τ 2.83 (9H, m, ArH), 7.61 and 7.83 (2H, AB quartet, *J* 13 Hz, CH₂), 8.33 (3H, s, Me), 8.67 (3H, s, Me), and 8.97 (3H, s, Me).

Reactions in the presence of acetic acid were carried out in the same way.

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¹⁶ R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *J. Amer. Chem. Soc.*, 1963, **85**, 3984.
