

Organic Oxidation Processes. Part II. The Reaction of Lead Tetra-acetate with Toluene and Related Compounds.*

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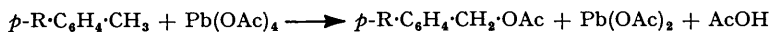
[Reprint Order No. 5449.]

The oxidation of toluene, of a series of *p*-substituted toluenes, and of ethylbenzene with lead tetra-acetate is described. The specific formation of benzyl acetates (i) is facilitated by electron-releasing and retarded by electron-attracting substituents, (ii) is independent of the solvent, and (iii) does not involve free benzyl or acetate radicals.

LEAD TETRA-ACETATE was first employed as an organic oxidant by Dimroth and Schweizer (*Ber.*, 1923, 56, 1375) who showed that it replaced hydrogen of an active methyl or methylene system by an acetoxy group. In particular, toluene was oxidised to benzyl acetate, and di- and tri-phenylmethane gave the corresponding arylmethyl acetates. We now report the reaction of lead tetra-acetate with various *para*-substituted toluenes and, for the first time, a systematic examination of the influence of substituents (OMe, Me, Bu^t, Br, and NO₂) is recorded for this oxidant (cf. Criegee, "Newer Methods of Preparative Organic Chemistry," Interscience Publ., New York, 1948, p. 6). In addition, these oxidations provide evidence on the mechanism of the reaction.

Dimroth and Schweizer (*loc. cit.*) obtained an 11% yield of benzyl acetate from toluene, using boiling acetic acid as solvent. Our oxidations have been carried out in acetic acid solution at 80°; reaction then proceeds at a satisfactory rate and decomposition of lead tetra-acetate is minimised. The yield of the *para*-substituted benzyl acetate increases (within experimental limits) with the increasing electron-releasing power of the substituent group: *p*-bromo- 5%, *p*-nitro-toluene 7%, toluene 25%, *p*-methyl- 47%, *p*-*tert*-butyl- 55%, and *p*-methoxy-toluene 60%. Benzyl acetate and the *p*-methoxy-, *p*-methyl, and *p*-*tert*-butyl derivatives were readily separated by fractionation under reduced pressure from the unchanged toluenes, which were recovered. The smaller proportional amounts of *p*-nitro- and *p*-bromo-benzyl acetate proved difficult to separate from the parent toluenes but saponification values gave the percentages of acetate listed above, and *p*-nitro- and *p*-bromo-benzyl alcohol were then isolated.

The synthetic possibilities of this oxidation process, in which toluenes yield solely benzyl acetates, merit attention. The overall reaction is :



That parent hydrocarbon is recovered indicates that some of the lead tetra-acetate suffers decomposition in acetic acid, even at 80°. [The decomposition of lead tetra-acetate has

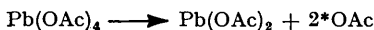
* Part I, *J.*, 1954, 2785.

been investigated recently by Kharasch, Friedlander, and Urry (*J. Org. Chem.*, 1951, **16**, 533) and by Mosher and Kehr (*J. Amer. Chem. Soc.*, 1953, **75**, 3172).]

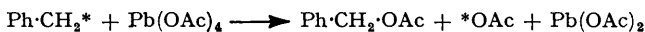
We have previously observed (Barron, Cavill, Cole, Gilham, and Solomon, *Chem. and Ind.*, 1954, 76) that the solvent can markedly influence the course of the lead tetra-acetate oxidation; *e.g.*, *p*-cresol yields 2 : 2-diacetoxy-4-methylcyclohexadienone in acetic acid, but 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl in benzene. Hence, in the present investigation, toluene and its *p*-methoxy- and *p*-nitro-derivative have also been oxidised in benzene, but only the benzyl acetate, and in the same yield, was obtained. Oxidation of toluene, in excess of substrate, yields benzyl acetate.

Oxidation of active methyl and methylene systems by lead tetra-acetate has been assumed to involve free-radical processes, especially as this oxidant is capable of yielding free acetate and methyl radicals (cf. Kharasch, Friedlander, and Urry, *J. Org. Chem.*, 1951, **16**, 533). Thus Dewar ("Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 277) proposed the following mechanism for the oxidation of toluene and similar compounds :

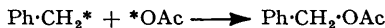
Initiation :



Propagation :



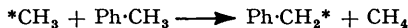
Termination :



Oxidation of toluene, at 80°, may be initiated by an acetate radical from the decomposition of lead tetra-acetate (as above) or, alternatively, an initial dehydrogenation by the more reactive methyl radical (from the decomposition of the acetate radical) takes place (cf. Waters, "The Chemistry of Free Radicals," Oxford Univ. Press, 1946, p. 231), *i.e.* :



and



In either case, propagation would then proceed by a chain mechanism involving free benzyl and acetate radicals. Finally, Dewar (*loc. cit.*) has indicated that only one termination reaction, *i.e.*, formation of benzyl acetate, should occur readily, and dimerisation of the mesomeric benzyl radicals to form dibenzyl would be relatively slow.

Whereas Kharasch *et al.* (*loc. cit.*) obtained a trace of succinic acid from the oxidative decomposition of boiling acetic acid with lead tetra-acetate, we have been unable to isolate any dimeric products from the oxidation of toluene or the more reactive *p*-methoxytoluene with this reagent. That we obtain only benzyl acetates, even on reaction in benzene solution (which solvent would favour dibenzyl formation, cf. Part I, *J.*, 1954, 2785), indicates the absence of free benzyl or *p*-methoxybenzyl radicals. Moreover, were acetate or methyl radicals (from the decomposition of acetate radicals) involved we would expect reaction in chloroform or carbon tetrachloride to show solvent interchange. For example, Wessely and Schinzel (*Monatsh.*, 1953, **84**, 425) isolated $\alpha\alpha\alpha$ -trichloro- β -(3 : 5-dimethyl-4-hydroxyphenyl)ethane after reaction of mesitol, in chloroform, with acetyl peroxide (which is well known to yield acetate and methyl radicals; cf. Kharasch and Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15). However, our reaction of *p*-methoxytoluene with lead tetra-acetate, in carbon tetrachloride, gave only *p*-methoxybenzyl acetate; no chlorinated derivative such as a trichloroethane, *p*-methoxybenzyl chloride, or hexachloroethane was detected.

The absence of solvent effects suggests that benzyl and acetate radicals are not involved in our lead tetra-acetate oxidations, and this is confirmed by a comparative reaction with acetyl peroxide. Toluene and *p*-methoxytoluene with acetyl peroxide in acetic acid readily yield dibenzyl and 4 : 4'-dimethoxydibenzyl respectively. Whether the dibenzyls result from a dehydrogenation of the toluene system by a methyl rather than an acetate

radical, does not influence the conclusion that this free-radical process differs vastly from the oxidations with lead tetra-acetate. Kharasch, McBay, and Urry (*J. Org. Chem.*, 1945, **10**, 401) have reported an analogous oxidation of ethylbenzene with acetyl peroxide, in excess of substrate, 2 : 3-diphenylbutane and higher polymeric products being formed. We have now shown that lead tetra-acetate readily converts ethylbenzene into the α -acetoxy-derivative, in excess of substrate or in acetic acid, no dimeric products being isolated.

Thus lead tetra-acetate oxidises the active methyl group of the toluene system by a process which (i) is more effective the greater the electron-releasing power of the *para*-substituent, (ii) is independent of the solvent, and (iii) does not involve free benzyl or acetate radicals. Probably the fundamental step is the formation, from the toluene and lead tetra-acetate, of a complex which breaks down to yield only the benzyl acetate, acetic acid, and lead acetate. Such a specific, though slow, reaction has obvious similarities with the glycol fission. (For recent discussions of the mechanism of glycol fission see Rigby, *J.*, 1950, 1907, and Cordner and Pausacker, *J.*, 1953, 102.)

EXPERIMENTAL

Oxidation of Toluene with Lead Tetra-acetate.—(a) Toluene (27.6 g.; freshly distilled over sodium) and lead tetra-acetate (133 g., prepared by method of Dimroth, Friedemann, and Kämmerer, *Ber.*, 1920, **53**, 481) in "AnalaR" acetic acid (120 ml.) were heated at 80° (oil-bath) until no positive test for the oxidant (starch-iodide) was obtained (54 hr.). After distillation of the acetic acid and unchanged toluene under reduced pressure, the residue was extracted with ether (3 × 50 ml.). Lead acetate remained. The ethereal solution was washed with water, sodium hydrogen carbonate solution, and water, then dried (MgSO₄). Removal of the solvent gave benzyl acetate (11.0 g., 25%) as a pale yellow oil, further purified by distillation, b. p. 222—223° (Found: C, 72.0; H, 6.75. Calc. for C₉H₁₀O₂: C, 72.0; H, 6.7%). Toluene (12.8 g.; b. p. 110°, n_D^{20} 1.4902) was recovered.

(b) Analogous oxidations of toluene in acetic acid-ether (equivalent solvent conditions to those employed for acetyl peroxide oxidation), in benzene, and in toluene gave benzyl acetate in yields of 21, 20, and 25% respectively.

No dibenzyl could be detected in any of the above reactions.

Oxidation of Toluene with Acetyl Peroxide.—Toluene (4.7 g.) in acetic acid (32 ml.) was added to acetyl peroxide (6.0 g.; Gambarjan, *Ber.*, 1909, **42**, 4003) in ether (150 ml.). The ether was distilled and the reaction mixture heated at 80° until no positive test for the oxidant (starch-iodide) was obtained (1 hr.). Excess of toluene and the acetic acid were removed by distillation, leaving a yellow oil (1.4 g.) which, on sublimation, yielded dibenzyl (0.2 g.). Further purification by chromatography from light petroleum on neutralised aluminium oxide, and resublimation, gave the compound as colourless plates, m. p. and mixed m. p. 50° (Found: C, 92.4; H, 7.9. Calc. for C₁₄H₁₄: C, 92.3; H, 7.7%). An unidentified oil remained.

Oxidation of Ethylbenzene with Lead Tetra-acetate.—(a) Ethylbenzene (10.6 g.; freshly distilled over sodium) and lead tetra-acetate (44.3 g.) in acetic acid (40 ml.) were heated at 80° until no positive test for the oxidant was obtained (16 hr.). The mixture, worked up as described for toluene, gave α -methylbenzyl acetate (5.2 g., 32%) as a colourless oil, b. p. 215—216° (Found: C, 73.3; H, 7.4. Calc. for C₁₀H₁₂O₂: C, 73.2; H, 7.4%). Ethylbenzene (4.6 g.; b. p. 135—137°, n_D^{20} 1.4956) was recovered.

(b) Similar oxidation of ethylbenzene (26.5 g.) with lead tetra-acetate (44.3 g.) in the absence of added solvent gave α -methylbenzyl acetate (10.3 g., 63% based on the lead tetra-acetate) as a colourless oil, b. p. 213—217° (Found: C, 73.3; H, 7.5%). Unchanged ethylbenzene (13.7 g.; b. p. 136°, n_D^{20} 1.4958) was recovered.

Oxidation of p-Methoxytoluene with Lead Tetra-acetate.—(a) *p*-Methoxytoluene (36.6 g.; Korner, *Jahresber. Fortschv. Chem.*, 1867, 682) and lead tetra-acetate (133 g.) in acetic acid (120 ml.) were heated at 80° until no positive test for the oxidant was obtained (3 hr.). The mixture, after distillation of acetic acid under reduced pressure, was worked up as described for toluene. The yellow oil (38.1 g.), so obtained, was fractionated to give *p*-methoxytoluene (5.7 g.; n_D^{20} 1.5122) and *p*-methoxybenzyl acetate (32.4 g., 60%; n_D^{20} 1.5118) as a colourless oil, b. p. 150°/23 mm. (Found: C, 66.7; H, 6.6%; sap. val., 306, 300. Calc. for C₁₀H₁₂O₃: C, 66.7; H, 6.7%; sap. val., 311).

(b) Similar oxidations of *p*-methoxytoluene in benzene, and in carbon tetrachloride, gave the *p*-methoxybenzyl acetate in yields of 51 and 56% respectively. The unchanged *p*-methoxytoluene was recovered in each case and no 4 : 4'-dimethoxydibenzyl could be detected. The product from oxidation in carbon tetrachloride gave no test (Lassaigne's) for halogen.

Oxidation of p-Methoxytoluene with Acetyl Peroxide.—*p*-Methoxytoluene (6.0 g.) in acetic acid (37 ml.) was added to acetyl peroxide (6.0 g.) in ether (150 ml.). The mixture, treated as for toluene, gave a semisolid residue (2.2 g.). Distillation of this product yielded *p*-methoxytoluene (1.3 g.; n_D^{19} 1.5140; sap. val., 0) and a residual solid (0.8 g.), which after purification by chromatography gave 4 : 4'-dimethoxydibenzyl, finally isolated as colourless prisms, m. p. 124°, from ethanol (Found: C, 79.1; H, 7.7. Calc. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5%). Freund and Reitz (*Ber.*, 1906, **39**, 2219) record m. p. 125°.

Oxidation of p-Xylene and p-tert.-Butyltoluene.—(a) *p*-Xylene (10.6 g., freshly distilled over sodium) and lead tetra-acetate (44.3 g.) in acetic acid (40 ml.) were heated at 80° (30 hr.). The mixture, when treated as for toluene, gave *p*-methylbenzyl acetate (7.5 g., 47%), b. p. 227—230° (Found: C, 73.6; H, 7.4%; sap. val., 337. Calc. for $C_{10}H_{12}O_2$: C, 73.2; H, 7.4%; sap. val., 342), and *p*-xylene (4.3 g.; b. p. 138°, n_D^{20} 1.4955).

(b) Similar oxidation of *p*-tert.-butyltoluene (14.8 g.; Bialobrzewski, *Ber.*, 1897, **30**, 1773) with lead tetra-acetate (44.3 g.) in acetic acid (40 ml.) gave *p*-tert.-butyltoluene (5.2 g.; b. p. 64°/18 mm., n_D^{20} 1.4943) and *p*-tert.-butylbenzyl acetate (11.3 g., 55%), b. p. 142°/15 mm. (Found: C, 75.5; H, 8.7%; sap. val., 280. Calc. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%; sap. val., 272).

Oxidation of p-Nitro- and p-Bromo-toluene with Lead Tetra-acetate.—(a) *p*-Nitrotoluene (27.4 g., recrystallised from aqueous alcohol) and lead tetra-acetate (88.6 g.) in acetic acid (80 ml.) were heated at 80° (12 hr.). The mixture, worked up as described for *p*-methoxytoluene, but with chloroform for extraction, gave a yellow semisolid mass (28.7 g.) which contained mainly *p*-nitrotoluene and some *p*-nitrobenzyl acetate (7%, estimated by sap. value). The saponified mixture was then chromatographed on neutralised aluminium oxide; elution with light petroleum yielded *p*-nitrotoluene (23.4 g.; m. p. and mixed m. p. 50—51°), and with methanol-chloroform (10 : 90) gave *p*-nitrobenzyl alcohol (1.4 g.), finally isolated as yellow needles, m. p. and mixed m. p. 91—92° (from light petroleum).

(b) Similarly, *p*-nitrotoluene (13.7 g.) with lead tetra-acetate (44.3 g.) in benzene (110 hr., test for oxidant still positive) yielded recovered *p*-nitrotoluene (10.0 g.), m. p. and mixed m. p. 51°, and *p*-nitrobenzyl alcohol (0.3 g.), m. p. and mixed m. p. 91°. 4 : 4'-Dinitrodibenzyl was not detected.

(c) *p*-Bromotoluene (17.1 g., purified by distillation over sodium) with lead tetra-acetate (44.3 g.) in acetic acid (40 ml.) was heated at 80° for 110 hr., the test for oxidant being still positive. The mixture, worked up as described in (a) but with ether for extraction, gave recovered *p*-bromotoluene (10.0 g.), m. p. and mixed m. p. 26—27°, and *p*-bromobenzyl alcohol (0.5 g.), pale yellow needles, m. p. and mixed m. p. 76—77° (from light petroleum). The sap. value, before chromatography, indicated 5% of *p*-bromobenzyl acetate.

Dr. E. Challen is thanked for micro-analyses.

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[Received, June 8th, 1954.]