434. *The Reaction of Lead Tetra-acetate with Chlorobenzene and Ethyl Benzoate.*

By D. I. Davies.

The reaction of lead tetra-acetate with chlorobenzene and ethyl benzoate is shown to involve an initial free-radical methylation followed by conversion of the methyl into $CH_2{\cdot}OAc$ by a process which could involve two-multimembered transition states.

Dimroth and Schweizer,[1] treating toluene with lead tetra-acetate in boiling acetic acid, obtained an 11% yield of benzyl acetate. Fieser *et al.*[2] showed that lead tetra-acetate methylates aromatic nitro-compounds in acetic acid on the steam-bath; benzene, however, gave benzyl acetate and no toluene; chlorobenzene gave 4-chlorobenzyl acetate and perhaps other isomers but no chlorotoluene. The formation of benzyl acetate from toluene was envisaged by Dewar[3] as a free-radical process involving benzyl radicals. However benzyl radicals readily dimerise to give bibenzyl,[4] and Cavill and Solomon,[5] failing to find it, concluded that benzyl and acetate radicals are not involved.

Reinvestigation has now shown that chlorobenzene and lead tetra-acetate give both chlorotoluenes and chlorobenzyl acetates, which indicates methylation as the first stage, followed by formation of chlorobenzyl acetates. The $o : (m + p)$ ratio for the chlorotoluenes was found by vapour-phase chromatography; the chlorotoluenes were then oxidised by potassium permanganate to chlorobenzoic acids under conditions not affecting the isomer ratio, and these were then converted into methyl esters by diazomethane. The $m : p$ ratio was obtained from the nuclear magnetic resonance spectrum of the mixed chlorobenzoates. The chlorobenzyl acetates, on hydrolysis, gave the alcohols which were oxidised to the chlorobenzoic acids and converted into methyl chlorobenzoates, and the $o : (m + p)$ and the $m : p$ ratio then obtained by vapour-phase chromatography and nuclear magnetic resonance, respectively. The results (Table 1) may be compared with those for some other types of substitution in chlorobenzene, as shown in Table 2.

Table 1.

Isomer ratios for the chlorotoluenes and chlorobenzyl acetates obtained by reaction of chlorobenzene with lead tetra-acetate.

Expt.	Chlorotoluenes			Chlorobenzyl acetates		
no.	$o : (m + p)$	$m : p$	$o : m : p$	$o : (m + p)$	$m : p$	$o : m : p$
1	68 : 32	40 : 60	68 : 13 : 19	58 : 42	37 : 63	58 : 16 : 26
2	68 : 32	42 : 58	68 : 13 : 19	59 : 41	36 : 64	59 : 15 : 26

Table 2.

Isomer ratios for substitution reactions of chlorobenzene.

Reaction	o	m	p	Ref.	Reaction	o	m	p	Ref.
Methyln., $Bu^t_2O_2$	64	25	11	6	Introdn. BzO, $AgBr(OBz)_2$	36	13	51	9
,, MeHgI	62	28	10	7	Nitration, $AcNO_3$–$MeNO_2$	30	1	69	10
Phenyln., Bz_2O_2	50	32	18	8					

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[1] Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375.

[2] Fieser, Clapp, and Daudt, *J. Amer. Chem. Soc.*, 1942, **64**, 2052.

[3] Dewar, "Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 277.

[4] Johnston and Williams, *J.*, 1960, 1168.

[5] Cavill and Solomon, *J.*, 1954, 3943.

[6] Cowley, Norman, and Waters, *J.*, 1959, 1799.

[7] Corbett and Williams, *Proc. Chem. Soc.*, 1961, 240.

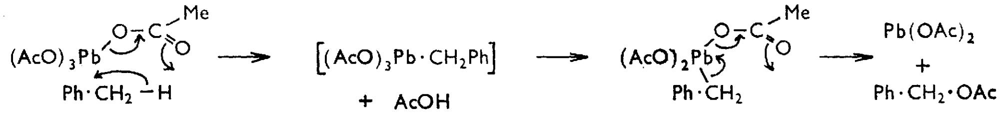
[8] Chang Shih, Hey, and Williams, *J.*, 1958, 2600.

[9] Bryce-Smith and Clarke, *J.*, 1956, 2264.

[10] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

Reaction of lead tetra-acetate with ethyl benzoate gave a mixture of ethyl toluates as major product, with a small amount of higher-boiling material which partly decomposed on distillation and probably contained some of the benzyl acetates. The isomer ratio for the ethyl toluates was obtained by vapour-phase chromatography of their ethyl benzoate solution; two experiments gave identical results: $o : m : p = 68 : 10 : 22$. Phenylation of methyl benzoate with benzoyl peroxide,[11] and nitration of ethyl benzoate by acetyl nitrate[12] gave ratios 58 : 17 : 25 and 24 : 74 : 4, respectively.

The predominant *ortho/para*-substitution for both chlorobenzene and ethyl benzoate indicates the free-radical nature of the first step of the reaction which involves the introduction of a methyl group: it is clearly not an electrophilic substitution. The second stage is the conversion of the methyl group into $CH_2{\cdot}OAc$, and if this were free-radical in nature benzyl radicals would be involved, giving bibenzyl as a by-product owing to their ready dimerisation. Cavill and Solomon[5] report that lead tetra-acetate and toluene give no bibenzyl, and we have confirmed this, using vapour-phase chromatography. It might be thought that any benzyl radicals formed would react with acetic acid to give benzyl acetate before they could dimerise, and some support was given by the observation that lead tetra-acetate and propionic acid react with toluene to give a mixture of benzyl acetate and propionate. This, however, could also be due to an exchange between lead tetra-acetate and propionic acid. The reaction of di-t-butyl peroxide with toluene is known to give bibenzyl through the intermediacy of benzyl radicals,[4] and this reaction, conducted in the presence of an excess of acetic acid, gave bibenzyl and no benzyl acetate. It is thus clear that the second stage of the reaction does not involve free radicals and it is proposed that two multi-membered transition states are involved and that the reaction takes place as illustrated.



Similar transition states are well established for certain other reactions of lead tetra-acetate (for a review see Criegee[13]). The methyl radicals involved in the first stage of the reaction must arise by loss of carbon dioxide from acetate radicals produced on thermal decomposition of lead tetra-acetate. However, it is unlikely that the methyl radical ever becomes entirely free, since it might then abstract a hydrogen atom from a methyl group of an already formed toluene or chlorotoluene to give a benzyl radical which could then dimerise. Consequently it is probably still closely associated with the lead of its parent molecule. If the radical were partially bonded to the lead it would be more electrophilic in character and this could account for the greater amount of *para*- than of *meta*-substitution in the formation of chlorotoluenes and chlorobenzyl acetates, for this is the inverse of the ratio in substitution by methyl radicals from di-t-butyl peroxide or methylmercuric iodide. The predominant *ortho*-substitution of chlorobenzene and ethyl benzoate may indicate an initial association of the lead tetra-acetate with the electron-rich chlorine atom and ethoxycarbonyl group before the substitution stage. In the conversion of the chlorotoluenes into chlorobenzyl acetates the isomer ratios indicate that reaction is effected slightly less readily at the *ortho*-position, which might be explained on the basis of enhanced stability of the methyl group in that position due to hydrogen bonding to chlorine.

EXPERIMENTAL

The nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 machine. Vapour-phase chromatography was carried out with a Perkin-Elmer model 116T instrument

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[11] Saunders, Ph.D. Thesis, London, 1958.

[12] Ingold and Smith, *J.*, 1938, 905.

[13] Criegee, *Angew. Chem.*, 1958, **70**, 173.

and helium, with columns on Celite (60—100 mesh) [(A) 1 m. "O"-30% silicone grease; (B) 2 m. "O"-30% silicone grease; (C) 3 m. "K"-30% "Carbowax" polyethylene glycol (*M* 1500)], or with a Pye argon chromatograph and the 4 ft. columns of Celite (100—120 mesh) [(D) 15% dinonyl phthalate; (E) 15% silicone grease with 1·5% of sodium hexanoate; (F) 15% Apiezon L grease]

The methods used in the determination of isomer ratios were shown to give results accurate to ±5% by analysis of mixtures of known composition after other mixtures of known composition had been used to calibrate peak areas and/or heights. Conversion of the type chlorotoluenes $\longrightarrow$ chlorobenzoic acids $\longrightarrow$ methyl chlorobenzoates were also shown to have little effect on the isomer ratios.

Reaction of Chlorobenzene with Lead Tetra-acetate in Acetic Acid.—A mixture of chlorobenzene (58·3 ml.), lead tetra-acetate (25 g.), and glacial acetic acid (50 ml.) was heated under reflux. A yellow solution soon resulted and much gas was evolved. The reaction was complete after 4 hr. The mixture was then diluted with water (100 ml.), and the chlorobenzene layer separated off. The aqueous layer was extracted with benzene (4 × 50 ml.), and the extracts were added to the chlorobenzene layer. This organic mixture was extracted with saturated sodium hydrogen carbonate solution (4 × 50 ml.) to remove acetic acid, washed with water (2 × 25 ml.), and dried (Na_2SO_4). Distillation at a slightly reduced pressure served to remove most of the benzene and chlorobenzene. These fractions were shown to contain no chlorotoluenes, by vapour-phase chromatography on column (B) at 180°. The chlorotoluenes, together with some chlorobenzene, were then distilled in a 10-ml. fraction, b. p. 60—100°/20 mm., which was estimated by vapour-phase chromatography, as above, to contain 10% of chlorotoluenes. The solution was analysed on column (D) at 82°, with a gas pressure of 7 lb./sq. in. and a flow rate of 60 ml./min. *o*-Chlorotoluene had a retention time of 24·2 min. and (*m* + *p*)-chlorotoluene one of 26·5 min.

The chlorotoluene solution was boiled overnight with potassium permanganate (2·5 g.) and sodium carbonate (1 g.) in water (100 ml.), and the isolated chlorobenzoic acids were converted into their methyl esters by diazomethane. The $m:p$ ratio was measured from the relative heights of the nuclear magnetic resonance signals of the mixture at 7·91 and 7·83 τ due solely to the *meta*- and the *para*-isomer, respectively.

The material left after distillation of the chlorotoluenes had b. p. 110—120°/10 mm. and was a mixture of chlorobenzyl acetates (Found: C, 58·4; H, 5·0. Calc. for $C_9H_9ClO_2$: C, 58·55; H, 4·9%). Boiling it for 4 hr. with potassium hydroxide (5 g.) in water (50 ml.) gave chlorobenzyl alcohols which were oxidised to chlorobenzoic acids with potassium permanganate and sodium carbonate as above, and converted into methyl chlorobenzoates with diazomethane. The $o:(m+p)$ ratio for the methyl esters was found by vapour-phase chromatography on column (C) at 180° (gas pressure 1·5 kg./cm.^{2}; flow rate 62 ml./min.). The retention time for the *ortho*-isomer was 45·5 min. and for the (*meta* + *para*)-isomers 32·5 min. The yields of the various products for experiments 1 and 2 were: PhCl–C_6H_4MeCl, 8·2, 9·8 g.; C_6H_4MeCl (estimated) 10, 9%; $C_6H_4Cl{\cdot}CH_2{\cdot}OAc$, 1·48, 1·74 g.; $C_6H_4Cl{\cdot}CO_2H$ (from C_6H_4MeCl), 0·55, 0·53 g., $C_6H_4Cl{\cdot}CH_2{\cdot}OH$, 0·67, 0·82 g.; $C_6H_4Cl{\cdot}CO_2H$ (from $C_6H_4Cl{\cdot}CH_2{\cdot}OH$), 0·70, 0·92 g.

Reaction of Ethyl Benzoate with Lead Tetra-acetate in Acetic Acid.—Ethyl benzoate (80·46 ml.), lead tetra-acetate (25 g.), and acetic acid (50 ml.) were heated at 140°. A solution was soon obtained, much gas was evolved, and the reaction was complete in 4 hr. The mixture was worked up as described in the preceding section. The ethyl benzoate and toluates co-distilled and were removed in about 80 ml. of distillate boiling up to 70°/0·1 mm. The isomer ratios for the ethyl toluates (yield 4 g. in each of two experiments) were obtained by injection of samples of their ethyl benzoate solution on to column (E) at 96° (flow rate 43 ml./min., argon pressure 7 lb./sq. in.). The retention times were 23·8, 30·7, and 32·5 min., for the *ortho*-, *meta*-, and *para*-isomer, respectively. The material (1·33 g.) remaining after distillation of this fraction had b. p. 70—110°/0·1 mm. It tended to decompose on distillation and on vapour-phase chromatography and was discarded.

Reaction of Lead Tetra-acetate with Toluene.—Toluene (60 ml.), lead tetra-acetate (25 g.), and acetic acid (50 ml.) were heated for 3 days on a boiling-water bath. The mixture was worked up in the usual way. The material with b. p. 110°/10 mm. (1 g.) was shown by vapour-phase chromatography on column (B) at 203° to be a mixture of benzyl acetate and methylbenzyl acetates. No bibenzyl was detected. A similar result was obtained in the absence of acetic acid.

Reaction of Lead Tetra-acetate with Toluene in the Presence of Propionic Acid.—Toluene (60 ml.), lead tetra-acetate (25 g.), and propionic acid (50 ml.) were heated on a boiling-water bath for 2 days. After the usual working up, vapour-phase chromatography on column (A) at 168° showed that benzyl propionate was the major product although benzyl acetate was also present. Hydrolysis of the benzyl propionate gave benzyl alcohol and propionic acid. The latter was characterised as its *S*-benzylisothiouronium salt, m. p. and mixed m. p. 149°.

Reaction of Di-t-butyl Peroxide with Toluene and Acetic Acid.—Acetic acid (50 ml.), toluene (60 ml.), and di-t-butyl peroxide (8·3 g.) were refluxed for 3 days and, after the usual working up and removal of the excess of toluene, the residue was distilled (b. p. 80—90°/0·1 mm.; 2·3 g.). It was bibenzyl and had m. p. and mixed m. p. 52° after recrystallisation. Vapour-phase chromatography of the crude distillate on column (F) at 164° showed the presence of bibenzyl and absence of benzyl acetate.

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Department of Organic Chemistry,
The University, Leeds, 2.

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