Homolytic Aromatic Substitution. Part VI. Lead Tetrabenzoate—a New Phenylating Agent.*

By D. H. Hey, C. J. M. Stirling, and G. H. Williams.

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Lead tetrabenzoate reacts with chlorobenzene and with nitrobenzene at 130° to give mixtures of the isomeric chlorodiphenyls and nitrodiphenyls respectively. The ratio of the isomers formed in the phenylation of nitrobenzene by lead tetrabenzoate is similar to that formed in the corresponding reaction with benzoyl peroxide. Lead tetrabenzoate effects the fission of vicinal glycols, whereas with benzoyl peroxide oxidation to ketonic products results. The mechanisms of these reactions are briefly discussed.

Fieser and Chang (*J. Amer. Chem. Soc.*, 1942, **64**, 2043) have shown that salts of quadrivalent lead with aliphatic acids can act as alkylating agents for α-naphthaquinones. In this manner 2-methyl-1 : 4-naphthaquinone was converted by lead tetra-acetate into 2 : 3-dimethyl-1 : 4-naphthaquinone, with evolution of carbon dioxide, in yields as high as 50% by operating in boiling acetic acid or at lower temperatures in the presence of a promoter, such as malonic acid, ethyl acetoacetate, or methanol. Similar reactions could be effected by the use of red lead, a promoter, and the appropriate acid. The reaction was applied to the introduction of several alkyl groups, of the benzyl group, and of the phenethyl group. In a subsequent publication (Fieser, Clapp, and Daudt, *ibid.*, p. 2052) it was shown that lead tetra-acetate was also capable of effecting the methylation of aromatic nitro-compounds and the reaction with nitrobenzene gave a mixture of *o*- and *p*-nitrotoluene. Similar reactions with benzene and chlorobenzene gave benzyl and chlorobenzyl acetates by successive methylation and acetoxylation, whereas naphthalene gave only 1-acetoxynaphthalene. These workers recognised the general resemblance between these reactions and (*a*) the electrolytic decomposition of sodium acetate in the Kolbe synthesis and (*b*) the reactions of acetyl peroxide. The intervention of free methyl radicals was considered and the suggestion was made that lead tetra-acetate might break down into lead diacetate and acetyl peroxide. Such acyl peroxides were shown to be excellent reagents for the alkylation of quinones (Fieser and Oxford, *ibid.*, p. 2060). In spite of the known phenylating action of benzoyl peroxide (Gelissen and Hermans, *Ber.*, 1925, **58**, 285; Hey, *J.*, 1934, 1966; Hey and Walker, *J.*, 1948, 2213) no work appears to have been carried out on lead tetrabenzoate as a potential phenylating agent.

The acceptance of common mechanisms to account for the reactions of lead tetra-acetate and acetyl peroxide has been questioned by Kharasch, Friedlander, and Urry (*J. Org. Chem.*, 1951, **16**, 533), who pointed out that the decomposition of lead tetra-acetate is dependent upon the solvent present and that the products obtained with these two compounds are frequently not strictly comparable. In particular, the reaction of a vicinal glycol with lead tetra-acetate results in the cleavage of a carbon–carbon bond, whereas with acetyl peroxide oxidation takes place to give a hydroxy-ketone and a diketone (*idem, ibid.*, 1949, **14**, 91). A comparison of the reactions of (*a*) lead tetra-acetate and (*b*) acetyl peroxide with acetic acid and with *iso*propyl ether revealed marked differences in the nature and proportions of the products formed, and these were attributed to a fundamental difference in mechanism. Whereas acetyl peroxide appeared

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* Part V, *J.*, 1954, 794.

to react by predissociation into free radicals, lead tetra-acetate was considered to undergo a bimolecular reaction with the solvent, and the logical consequences of these assumptions were shown to be consistent with the differences in product distribution observed in the two reactions. Both reactions, however, were considered to be of homolytic character.

The oxidation of vicinal glycols by lead tetra-acetate, however, is quite distinct and does not involve the liberation of either carbon dioxide or methane. It proceeds at relatively low temperatures and does not involve free radicals. It thus appears that there is adequate experimental evidence to indicate that the reactions of lead tetra-acetate can follow either a heterolytic or a homolytic course according to environmental circumstances (cf. Cordner and Pausacker, *J.*, 1953, 102; Mosher and Kehr, *J. Amer. Chem. Soc.*, 1953, **75**, 3172; Barron, Cavill, Cole, Gilham, and Solomon, *Chem. and Ind.*, 1954, 76). In the present communication the reactions of lead tetrabenzoate have been investigated with particular reference to some of the known reactions of benzoyl peroxide.

Lead tetrabenzoate was first prepared by Criegee (*Annalen*, 1930, **481**, 263), who reported its reaction with *cyclo*pentadiene at 35° to give the dibenzoate of *trans*-3-*cyclo*pentene-1 : 2-diol. Hurd and Austin (*J. Amer. Chem. Soc.*, 1931, **53**, 1543) modified Criegee's preparation; their product probably contained benzene of crystallisation and, on pyrolysis, gave a resinous mass from which lead dibenzoate and benzoic acid were separated. Elming and Clauson-Kaas (*Acta Chim. Scand.*, 1952, **6**, 535) have reported that furan and lead tetrabenzoate in benzene solution at 75° give 2 : 5-dibenzoyloxy-2 : 5-dihydrofuran. It is now shown that the decomposition of lead tetrabenzoate in chlorobenzene at 130° results in the formation of a mixture of isomeric chlorodiphenyls by nuclear phenylation. A similar reaction with nitrobenzene gave a mixture of isomeric nitrodiphenyls. In the former reaction the presence of 4-chlorodiphenyl in the product was proved by its conversion into 4-bromo-4′-chlorodiphenyl, and from the latter reaction both 2- and 4-nitrodiphenyl were isolated. Moreover, the exact composition of the mixture of nitrodiphenyls obtained from the reaction between lead tetrabenzoate and nitrobenzene was shown by means of ultra-violet spectrophotometry to be 55% *ortho*, 16% *meta*, and 29% *para*. A comparable reaction carried out under identical conditions with benzoyl peroxide in place of lead tetrabenzoate gave 56·3% *ortho*, 15·7% *meta*, and 28·0% *para*. The figures for the reaction with benzoyl peroxide now given refer to the reaction at 125° and the slightly different figures previously reported (Hey, Nechvatal and Robinson, *J.*, 1951, 2892), namely, 59·5% *ortho*, 10·0% *meta*, and 30·5% *para* (mean values), refer to the reaction carried out at 80°. It is thus clear that the phenylating action of lead tetrabenzoate follows closely the pattern observed with benzoyl peroxide and the various diazo-derivatives discussed by Hey, Nechvatal, and Robinson (*loc. cit.*). At 125° lead tetrabenzoate reacts by the liberation of benzoyloxy-radicals which by subsequent loss of carbon dioxide provide phenyl radicals.

On the other hand, a comparison of the reactions of lead tetrabenzoate and of benzoyl peroxide with butane-2 : 3-diol reveals the same contrast which is shown between lead tetra-acetate and acetyl peroxide (Kharasch, Friedlander, and Urry, *locc. cit.*). Butane-2 : 3-diol reacts rapidly with lead tetrabenzoate at 15° to give acetaldehyde in at least 78% yield. With benzoyl peroxide no reaction takes place in the cold, and at temperatures above 80° the product contains diacetyl and acetoin but no acetaldehyde. The glycol fission by both the tetra-acetate and the tetrabenzoate is a specific reaction which does not appear to involve free radicals (cf. Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159; Waters, in Gilman's " Organic Chemistry," Vol. IV, J. Wiley & Sons, N.Y., 1953, p. 1189) but the high-temperature reaction between a vicinal glycol and either acetyl or benzoyl peroxide shows the general features of a homolytic process. This interpretation of the reaction between benzoyl peroxide and a vicinal glycol is supported by the isolation of benzene, diphenyl, and diphenyl-4-carboxylic acid from the products of the reaction.

EXPERIMENTAL

Reagents.—Nitrobenzene (" AnalaR ") was washed with concentrated aqueous sodium hydroxide, then with water, and distilled with steam. After being dried ($CaCl_2$) it was fractionally frozen six times. Chlorobenzene was fractionally distilled from phosphoric oxide and collected at 132°/760 mm. Butane-2 : 3-diol was fractionally distilled and collected at 86—90°/20 mm. (n_D^{20} 1·4363). Methylene chloride was dried (P_2O_5) and distilled before use.

Lead tetrabenzoate was prepared by a modification of Criegee's method (*loc. cit.*). Lead tetra-acetate (50 g.), prepared by Bailar's method (*Inorg. Synth.*, 1939, **1**, 47), was added with shaking to molten benzoic acid (60 g.) at 130°. When the addition was complete the liberated acetic acid was removed at 40 mm. The solid residue, when cold, was broken up and thoroughly extracted with sodium-dried ether to remove free benzoic acid. The dry product (80 g.), after three crystallisations from dry (P_2O_5) methylene chloride, melted at 185° with decomposition. This product contained methylene chloride which was removed by heating at 100° for 3 hr. at 0·01 mm. to give a solvent-free compound as a pale yellow amorphous powder, m. p. 176° (decomp.) (Criegee, *loc. cit.* reported m. p. 168°). A specimen, m. p. 185°, recrystallised from chlorobenzene, gave the following analysis : C, 51·55; H, 3·45; Cl, 5·3. [Calc. for $4Pb(O{\cdot}CO{\cdot}Ph)_4,5C_6H_5Cl$: C, 51·2; H, 3·2; Cl, 5·3%]. The product was stored in a desiccator over phosphoric oxide.

The purity of successive batches of lead tetrabenzoate was determined iodometrically as follows : to a solution of lead tetrabenzoate (*ca.* 0·3 g.) in acetic acid (25 c.c.) was added a volume of aqueous potassium iodide (containing 9·6 g. of KI, 50 g. of Na_2CO_3, and 45 g. of NaOAc per litre) such that the potassium iodide was equivalent to the weight of the tetrabenzoate taken, assumed to be 100% $Pb(O{\cdot}CO{\cdot}Ph)_4$. The iodine liberated, which corresponds to 2 atoms per mol. of lead tetrabenzoate, was titrated with 0·05N-thiosulphate. The validity of the method was checked by microanalytical estimations for carbon and hydrogen.

Decomposition of Lead Tetrabenzoate in Chlorobenzene.—Lead tetrabenzoate (17 g.), crystallised from and containing chlorobenzene (2·6 g.), was dissolved in warm chlorobenzene (150 g.), and the solution was boiled under reflux. The solution darkened and after 45 hr. the decomposition was complete as shown by a negative starch–iodide test. Lead benzoate was filtered off from the cold mixture, and free benzoic acid was extracted with aqueous saturated sodium hydrogen carbonate (3 × 75 c.c.). The mixture was then washed with water and dried ($CaCl_2$). Chlorobenzene was removed by distillation through a 25 cm. helix-packed column, and esters in the residue (15 ml.) were hydrolysed for 4 hr. with 100 c.c. of boiling ~2N-sodium hydroxide. The unsaponifiable material was thoroughly extracted with benzene, and the benzene extracts, after being dried ($CaCl_2$), were chromatographed on an alumina column (2 × 25 cm.) and eluted with the benzene washings of the calcium chloride (100 c.c.) and ether (100 c.c.). Ether and benzene were removed from the combined eluates by distillation through a 25 cm. helix-packed column, and subsequent distillation of the residue by the method described by Augood, Hey, and Williams (*J.*, 1952, 2094) gave a mixture of chlorodiphenyls as a colourless oil (1·8 g.), b. p. 60—94°/0·2 mm. (Found : C, 76·7; H, 5·1; Cl, 18·3. Calc. for $C_{12}H_9Cl$: C, 76·4; H, 4·8; Cl, 18·8%). Bromination with a solution of bromine in acetic acid at 100° gave 4-bromo-4′-chlorodiphenyl, m. p. and mixed m. p. 154—155° after crystallisation from alcohol (cf. Hey, *J.*, 1934, 1968).

Decomposition of Lead Tetrabenzoate in Nitrobenzene.—(i) *Qualitative.* Lead tetrabenzoate (17·3 g.) was added with vigorous stirring to nitrobenzene (220 c.c.) at 130°. The solution darkened rapidly and stirring was continued until all the tetrabenzoate had dissolved. Heating was continued at 130° until decomposition was complete. Lead dibenzoate did not separate from the cold mixture but was precipitated by the addition of water, and filtered off. Except that nitrobenzene was removed at reduced pressure (20 mm.), the working-up was the same as that described for the decomposition in chlorobenzene. The final distillation, as in the preceding example, gave a pale yellow oil (1·9 g.) which partly solidified, b. p. 95—100°/0·2 mm. (Found : C, 72·7; H, 4·8; N, 7·15. Calc. for $C_{12}H_9O_2N$: C, 72·5; H, 4·5; N, 7·0%). A portion of this product (1 g.) in light petroleum (200 c.c.; b. p. 40—60°) was poured down an alumina column (2 × 25 cm.). Elution with the same solvent, followed by recrystallisation, gave first 2-nitrodiphenyl, m. p. and mixed m. p. 36·5°, and then 4-nitrodiphenyl, m. p. and mixed m. p. 110—112°.

(ii) *Quantitative.* Reactions were carried out in duplicate in a thermostat maintained at 125° ± 0·1° by the method previously used by Augood, Hey, and Williams (*loc. cit.*). The reaction flasks containing the nitrobenzene (150 c.c.) were placed in the thermostat for 1 hr. before the addition of the lead tetrabenzoate. The addition of the tetrabenzoate (17·3 g.) was effected with vigorous stirring and then a further 50 c.c. of solvent were added dropwise. Stirring was continued for 1 hr. and the mixtures were removed from the thermostat after 15 hr., reactions being then complete. Duplicate reactions for comparison were carried out simultaneously with benzoyl peroxide (7·8 g.) in nitrobenzene (100 c.c.), under the same conditions of time and temperature. The working-up of the four mixtures was the same as that described for the qualitative experiments. Final distillation gave mixtures of nitrodiphenyls as a yellow semi-solid, b. p. 104—124°/0·3 mm., from the lead tetrabenzoate reaction, and as an orange-coloured semi-solid, b. p. 99—128°/0·4 mm., from the benzoyl peroxide reactions. The orange-colour of the latter was not removed by chromatography. Higher phenylated products were distilled from the residues in each case as red resins, b. p. *ca.* 200°/0·4 mm. The products obtained from these reactions are listed in Table 1. Analyses for nitrogen in the mixtures of isomeric nitrodiphenyls were as follows: lead tetrabenzoate reactions (i) 7·25, (ii) 7·35; benzoyl peroxide reactions (i) 7·30, (ii) 7·35 (Calc. for $C_{12}H_9O_2N$: N, 7·0%).

The percentage of benzoate radicals accounted for in Table 1 amounts to 80·5 for the lead tetrabenzoate reaction and 77·9 for the benzoyl peroxide reaction.

The determination of the isomer ratios of the products formed in these reactions was carried out by ultra-violet spectrophotometry with the aid of a " Unicam S.P. 500 " quartz spectrometer, the method of calculation previously described (Cadogan, Hey, and Williams, *J.*, 1954, 794) being used. The absorption curves of the pure isomers have been recorded by Pestemer and Mayer-Pitsch (*Monatsh.*, 1937, **70**, 104) and by De Tar and Scheifele (*J. Amer. Chem. Soc.*, 1951, **73**, 1442). The extinction coefficients of the two mixtures from the lead tetrabenzoate reactions differed only slightly and the mean was used for purposes of calculation. The mixtures from the benzoyl peroxide reactions were treated separately. The compositions of the mixtures thus obtained are given in Table 2, the overall error in each determination being ±2%.

TABLE 1. *Products obtained in reactions with nitrobenzene at* 125°.

	$Pb(O{\cdot}CO{\cdot}Ph)_4$ reaction		$(Ph{\cdot}CO{\cdot}O)_2$ reaction	
Product	g. (mean)	Mole/mole (mean)	g. (mean)	Mole/mole (mean)
Free $Ph{\cdot}CO_2H$	3·00	0·985	2·89	0·74
$Ph{\cdot}CO_2H$ from ester	0·53	0·17	0·45	0·11
$Ph{\cdot}C_6H_4{\cdot}NO_2$	2·13	0·43	4·15	0·65
Higher phenylated products	0·10	0·01 *	0·29	0·03 *

* Calculated as $Ph{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NO_2$.

TABLE 2. *Isomer ratios in reactions with nitrobenzene at* 125°.

	Isomers (%)		
Reaction	*ortho*	*meta*	*para*
Lead tetrabenzoate reaction (mean)	55	16	29
Benzoyl peroxide reaction (1)	57·4	15·4	27·2
Benzoyl peroxide reaction (2)	55·3	16·0	28·7
Benzoyl peroxide reaction (mean)	56·3	15·7	28·0

*Action of Lead Tetrabenzoate on Butane-*2 : 3-*diol*.—Butane-2 : 3-diol (9 g.) in dry dioxan (30 c.c.) was added dropwise to a suspension of lead tetrabenzoate (20·6 g.) in dry dioxan (50 c.c.) stirred vigorously at 15°, precautions being taken to avoid loss of acetaldehyde. The yellow colour of the tetrabenzoate gradually faded and the white dibenzoate formed dissolved after 1 hour's stirring. The clear solution was left overnight, diluted to 250 c.c. with water, and filtered. The residue of lead dibenzoate and benzoic acid was washed with water and the combined filtrates were made up to 2 l. The acetaldehyde was estimated gravimetrically as the dimedone derivative, which without crystallisation had m. p. and mixed m. p. 139—140° (anhydride, m. p. 176°), and corresponded to 78% of theory. The glycol could also be oxidised in 20% aqueous solution without hydrolysis of the lead tetrabenzoate (cf. Baer, Groscheintz, and Fisher, *J. Amer. Chem. Soc.*, 1939, **61**, 2607), which is evidence of a reaction even more rapid than the hydrolysis of the oxidising agent which occurs very readily.

*Action of Benzoyl Peroxide on Butane-*2 : 3-*diol*.—When the suspension of benzoyl peroxide (25 g.) in butane-2 : 3-diol (50 g.) was heated slowly to 80° under reflux a vigorous reaction started and the temperature rose to 140°. After the reaction had subsided the mixture was heated at 95° for 1 hr. Distillation gave : (i) a fraction, b. p. 80—100°/760 mm.. which contained diacetyl (semicarbazone, m. p. and mixed m. p. 272°) and benzene (*m*-dinitrobenzene, m. p. and mixed m. p. 90°), but no acetaldehyde (negative dimedone reaction); (ii) a fraction, b. p. 100°/760 mm. to 60°/20 mm., which contained acetoin (semicarbazone, m. p. 189°; osazone, m. p. and mixed m. p. 243°); and (iii) a fraction, b. p. 60—80°/20 mm., which contained diphenyl, m. p. and mixed m. p. 68°. The residue was dissolved in aqueous sodium hydroxide, washed with ether, and acidified in stages. The first acidic precipitate gave diphenyl-4-carboxylic acid, m. p. and mixed m. p. 224—225° after crystallisation from benzene–light petroleum (b. p. 60—80°); the subsequent precipitates consisted of benzoic acid, m. p. and mixed m. p. 120°.

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KING'S COLLEGE, UNIVERSITY OF LONDON,
STRAND, LONDON, W.C.2.

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