

Cyclisation Reactions Involving the Oxidation of Carboxylic Acids with Lead Tetra-acetate. Part III.¹ Oxidation of Phenyl- and *o*-Biphenyl-Substituted Acetic and Propionic Acids, and of *o*-Biphenylmethylmalonic Acid

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The lead tetra-acetate oxidation of phenylacetic acid and *o*-biphenylacetic acid gives, as major products, esters, the formation of which is suggested as proceeding *via* the intramolecular decomposition of intermediate lead(IV) salts. Appreciable formation of benzyl-type radicals in these reactions appears unlikely, since products unambiguously derived from such radicals are found in low yield. 3-Phenylpropionic acid and 3-(*o*-biphenyl)-propionic acid give rise to the corresponding phenethyl and *o*-biphenylethyl radicals. The former substitute in the solvent benzene, whereas the latter undergoes an intramolecular cyclisation to form 9,10-dihydrophenanthrene. Oxidation of *o*-biphenylmethylmalonic acid gives a good yield of phenanthrene, the formation of which *via* 9,10-dihydrophenanthrene-9-carboxylic acid is tentatively proposed.

THE lead tetra-acetate oxidation of toluene affords benzyl acetate $\text{PhCH}_2\cdot\text{OAc}$ (I) as major product;² however considerable controversy³ has arisen over the question of benzyl radicals as intermediates in the formation of this product. The lead tetra-acetate oxidation of benzene also gives rise to benzyl acetate (I),^{2a,3d} and it is very surprising that bibenzyl $\text{PhCH}_2\cdot\text{CH}_2\text{Ph}$ (II) and diphenylmethane PhCH_2Ph

(III), the usual products⁴ obtained when benzyl radicals are generated in benzene solution, are not formed. Although bibenzyl (II) is consumed, when oxidised with an excess of lead tetra-acetate in concentrated solution,^{3d} we find that reaction of bibenzyl (II) with lead tetra-acetate in dilute solution in benzene is very slow, and thus consumption of bibenzyl by lead tetra-acetate does

³ (a) M. J. S. Dewar, 'Electronic Theory of Organic Chemistry,' Oxford University Press, Oxford, 1949, p. 277; (b) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1954, 3943; (c) D. I. Davies, *J. Chem. Soc.*, 1963, 2351; (d) D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4860.

⁴ K. C. Bass, *Lab. Practice*, 1965, **14**, 47, 145; I. P. Gragerov and B. Z. Chizhov, *Russ. J. Org. Chem.*, 1966, **2**, 843.

¹ Part II, D. I. Davies and C. Waring, *J. Chem. Soc. (C)*, 1968, 1865.

² (a) O. Dimroth and R. Schweizer, *Chem. Ber.*, 1923, **56**, 1375; (b) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Amer. Chem. Soc.*, 1942, **64**, 2052.

not seem an adequate reason for the failure to find bibenzyl (II) as a product in the lead tetra-acetate oxidation of either benzene or toluene.

Free radicals have been established^{1,5-7} as intermediates in the oxidation of carboxylic acids with lead tetra-acetate, and in continuation of our studies^{1,6} (mole ratio of acid:lead tetra-acetate *ca.* 2:1, in benzene solution under nitrogen) we investigated the oxidation of phenylacetic acid $\text{PhCH}_2\text{CO}_2\text{H}$ (IV) since this should lead to the production of benzyl radicals. The major product formed was benzyl phenylacetate $\text{PhCH}_2\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ (V), together with much smaller quantities of benzyl acetate (I), bibenzyl (II), and

and benzyl phenylacetate (V). This is similar to the mechanism proposed by one of us^{3c} for the formation of benzyl acetate (I) in the lead tetra-acetate oxidation of toluene. Recently, after our work⁷ was completed, Kochi⁸ reported an extensive study of the lead tetra-acetate oxidation of phenylacetic acid (IV) under a variety of conditions, and demonstrated that toluene and benzaldehyde are formed in addition to the products found by us. The reaction under nitrogen is slow, and he observed that the effect of added catalysts is not completely typical^{5a,b} of the radical chain reaction found in his earlier studies on the oxidation of aliphatic carboxylic acids with lead tetra-acetate. Thus the

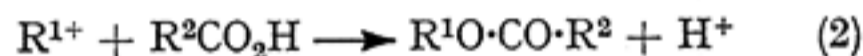
Quantities of reactants and yields of products

Acid (g.) (IV) (5.08)	Pb(OAc) ₄ (g.) 8.43	Benzene (ml.) 150	Reaction time (hr.) 96	Recovered acid (g.) 2.85	Product yields (g.; mole %/mole Pb(OAc) ₄)	
					Esters	Hydrocarbons
(VIII) (5.32)	5.46	150	72	1.49	(I) (0.06; 2.1)	(II) (0.10; 2.9)
(XIII) (4.27)	6.15	150	36	2.38	(V) (0.45; 10.5)	(III) (0.07; 2.2)
(XVI) (0.99)	0.98	100	2	0.60	(X) (0.47; 16.9)*	†
(XVII) (0.109)	0.098	50	1	0.056		(II) (1.81; 71)
(XX) (4.07)	5.90	150	1	2.99		(XVIII) (0.166; 41.7)
						(XIX) (trace)
						(XVIII) (not estimated)
						(XVIII) (0.001; 0.04)
						(XIX) (0.25; 10.5)

* Also 0.2 g. of unidentified product, possibly (XI). † 2-Methylbiphenyl a trace product.

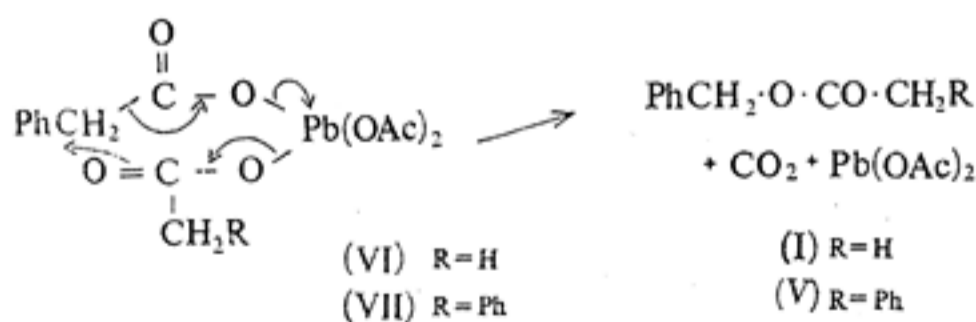
diphenylmethane (III) (See Table). The formation of these latter two products [(II) and (III)] is characteristic⁴ of the intermediacy of benzyl radicals, which may dimerise, or substitute in the solvent benzene. These products [(II) and (III)] are therefore not completely consumed, if consumed at all, by lead(IV) salts. Benzyl radicals are thus intermediates, even if of minor importance, in the lead tetra-acetate oxidation of phenylacetic acid (IV). The failure to find any bibenzyl (II) in the lead tetra-acetate oxidation of toluene,³ and bibenzyl (II) and diphenylmethane (III) in the lead tetra-acetate oxidation of benzene^{2a,3d} clearly indicates that benzyl radicals are not involved in these reactions, since the experiments with phenylacetic acid (IV) demonstrate that benzyl radicals can react, at least in part, by dimerisation and solvent substitution, even in the presence of lead(IV) salts. To account for the

general pathway, which we interpret as being a summary of his views on ester formation is not necessarily the



sole or even major route by which esters are formed in the oxidation of phenylacetic acid (IV). When phenylacetic acid (IV) and lead tetra-acetate are present in comparable amounts, ionic interchange is unlikely to proceed beyond $\text{Pb}^{\text{IV}}(\text{OAc})_3\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, so that statistically methyl is the most likely radical to be derived from this lead(IV) salt. When the ratio of phenylacetic acid (IV) to lead tetra-acetate is 8:1 most of the lead(IV) salt should be $\text{Pb}(\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ph})_4$, and benzyl should be the predominant radical formed. However, the results of Kochi⁸ show that such variations in reactant proportions have little effect on the yields of those products, bibenzyl (II) (shown to be stable under the reaction conditions) and diphenylmethane (III), derived unambiguously from benzyl radicals, whereas benzyl phenylacetate (V) is formed at the expense of benzyl acetate (I) when phenylacetic acid (IV) is present in large excess. It therefore seems unlikely that the esters and hydrocarbons have a common origin in the benzyl radical.

Kochi's work⁸ shows that in the lead tetra-acetate oxidation of acids, which are potential sources of benzyl-type radicals, the major products are esters, which are considered to be derived from benzyl-type radicals *via* benzyl-type carbonium ions [equations (1) and (2)]. On the other hand, when acids are oxidised which could



predominant ester formation in the oxidation of phenylacetic acid (IV) we suggest that ionic interchange between phenylacetic acid (IV) and lead tetra-acetate could result in the lead(IV) salts (VI) and (VII). These salts could undergo the intramolecular decomposition indicated, leading to the formation of benzyl acetate (I)

⁵ (a) J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **89**, 1811, 3609; (b) J. K. Kochi, J. D. Bacha, and T. W. Betha III, *J. Amer. Chem. Soc.*, 1967, **89**, 6538; (c) D. I. Davies and C. Waring, *Chem. Comm.*, 1965, 263.

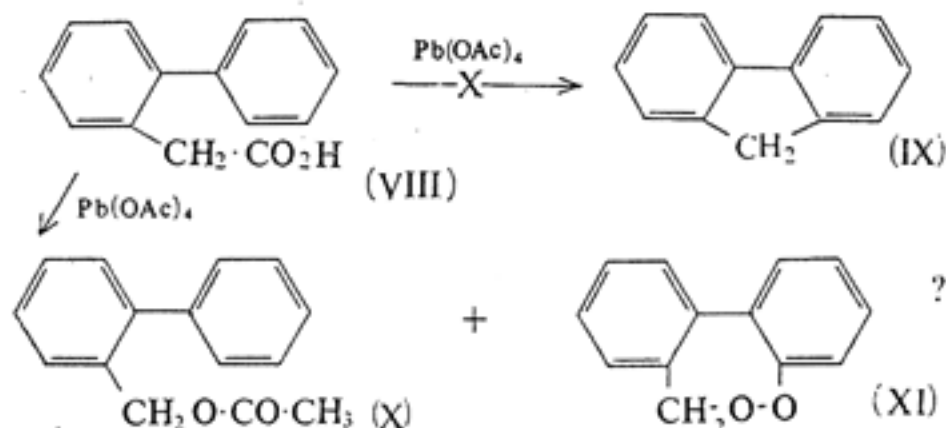
⁶ D. I. Davies and C. Waring, *J. Chem. Soc. (C)*, 1967, 1639.

⁷ C. Waring, Ph.D. Thesis, London, 1967.

⁸ J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1968, **33**, 83.

give rise to alkyl radicals^{5a,b} or aralkyl radicals^{1,8} (other than of the benzyl type), hydrocarbons derived from radical disproportionation, hydrogen abstraction, or solvent substitution are important products. Esters are never dominant, and are often only minor products. If the route to ester formation defined by equations (1) and (2) is invariably correct, then it implies that the oxidation of benzyl radicals is much readier than of alkyl radicals. However, as Kochi has pointed out⁸ the ionization potential of benzyl radicals^{9,10} is not significantly different from that of most secondary alkyl radicals.^{10,11} This fact coupled with the relatively slow oxidation of phenylacetic acid (IV) in the absence of catalysts,⁸ and the knowledge that heats of formation of benzyl radicals¹² are considerably greater than those of alkyl radicals,¹³ does tend to make our postulate somewhat attractive for the formation of esters in the lead tetra-acetate oxidation of phenylacetic acid (IV) by a route not involving benzyl radicals as intermediates. It must not be overlooked that ionization potentials, and heats of formation of benzyl and alkyl radicals, are derived from experiments in the gas phase. Thus, an extrapolation of these values to studies in solution must be made with caution. However in the nonpolar solvent benzene, solvation effects for the various radicals are unlikely to differ greatly, so that the comparison between gas phase and solution may well have appreciable significance.

Since hydrocarbon products derived directly from benzyl radicals are produced, albeit in low yield, from phenylacetic acid (IV), we extended our study to the oxidation of *o*-biphenylacetic acid (VIII) in the hope



that any *o*-biphenylmethyl radicals produced would give rise to fluorene (IX), the potential product of intramolecular cyclisation. However, fluorene (IX), 2,2'-diphenylbibenzyl, and 2-benzylbiphenyl, the major products to be expected from *o*-biphenylmethyl radicals, were not formed, suggesting that the *o*-biphenylmethyl radical may not be an important intermediate in this reaction. The major product is *o*-biphenylmethyl acetate (X), whose formation is most likely to occur by a route similar to the one we propose for ester formation from phenylacetic acid (IV). An additional product was shown by spectral evidence to have the

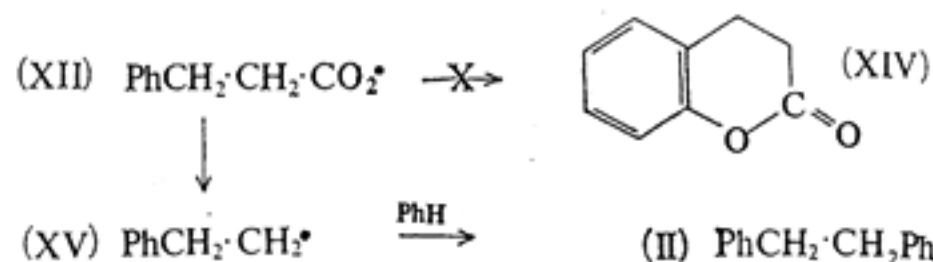
⁹ F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, 1954, **22**, 621; J. B. Farmer, I. H. S. Henderson, C. A. McDowell, and F. P. Lossing, *J. Chem. Phys.*, 1954, **22**, 1948.

¹⁰ D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31.

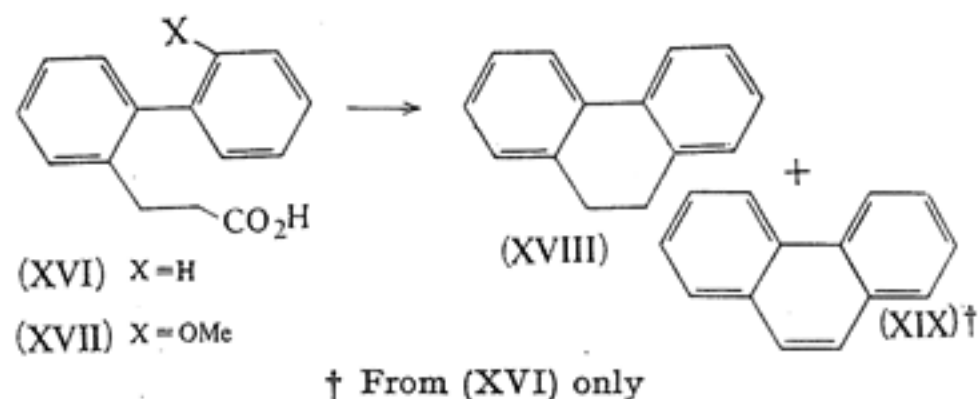
¹¹ J. B. de Sousa and F. P. Lossing, *J. Amer. Chem. Soc.*, 1959, **81**, 281.

grouping ArCH_2O . This evidence coupled with analytical data points to the cyclic peroxide (XI) as a possible structure.

The 3-phenylpropionoyloxy-radical (XII) is a potential intermediate in the oxidation of 3-phenylpropionic acid $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$ (XIII). The sole product we



could isolate from the reaction was bibenzyl (II) indicating that the radical (XII) undergoes decarboxylation to the 2-phenethyl radical (XV) before cyclisation to dihydrocoumarin (XIV) can occur. The 2-phenethyl radical then substitutes in the solvent benzene to give bibenzyl (II). Styrene, ethylbenzene, and phenethyl acetate are additional minor products when the reaction is conducted in benzene-acetic acid as solvent.⁸ The success of this reaction in producing 2-phenethyl radicals (XV) led us to study 3-(*o*-biphenyl)propionic acid (XVI), which afforded on lead tetra-acetate oxidation, as in the electrolysis,¹⁴ 9,10-dihydrophenanthrene (XVIII) the product of intramolecular cyclisation of 2-(*o*-biphenyl)ethyl radicals. A minor product was phenanthrene (XIX), thought to arise from 9,10-



dihydrophenanthrene (XVIII) *via* dehydrogenation, a known property of lead tetra-acetate.¹⁵ 9,10-Dihydrophenanthrene (XVIII) was also a product from the oxidation of 3-(*o*-methoxybiphenyl)propionic acid (XVII), a reaction which provides an example of the displacement of a methoxy-group by an alkyl radical. This may be compared with the oxidation of 2'-methoxybiphenyl-2-carboxylic acid, in which 3,4-benzocoumarin is formed by displacement of the methoxy-group by a carboxylate radical.⁶

Oxidation of *o*-biphenylmethylmalonic acid (XX) gave phenanthrene (XIX) as major product together with a little 9,10-dihydrophenanthrene (XVIII). Due to the close proximity of the carboxy-groups in *o*-biphenylmethylmalonic acid (XX), ionic interchange with lead tetra-acetate is likely to proceed to the lead(IV)

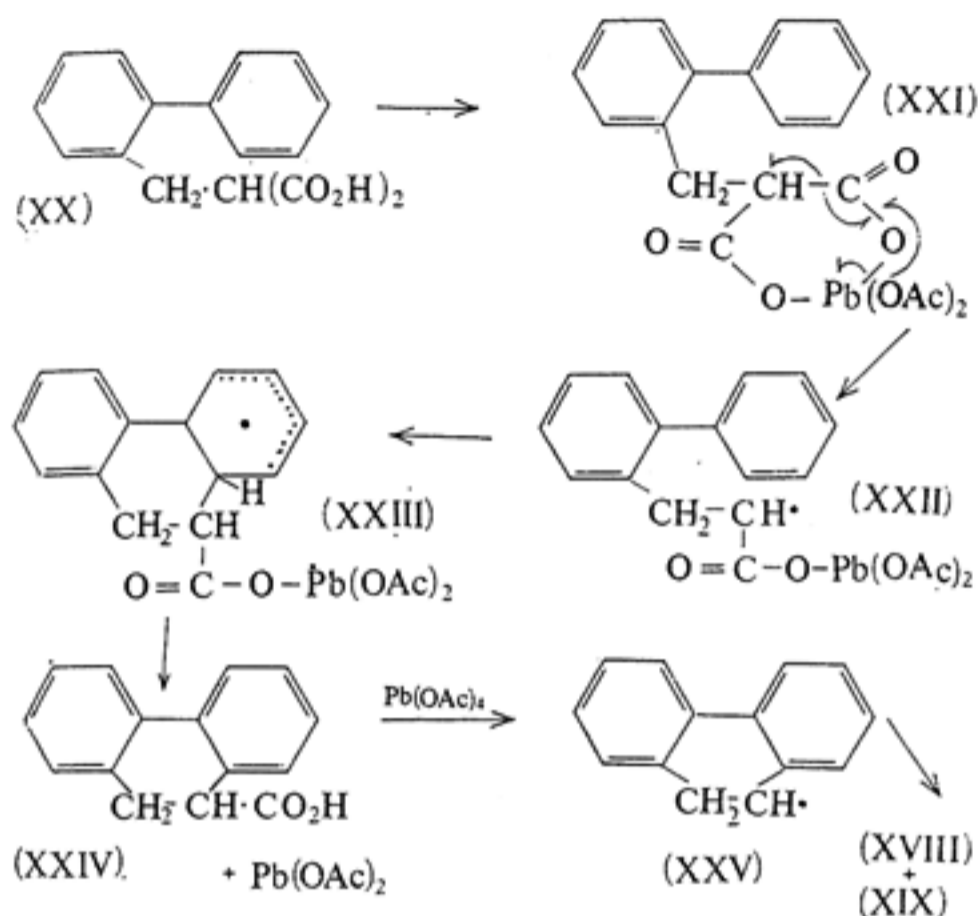
¹² S. W. Benson and J. H. Buss, *J. Phys. Chem.*, 1957, **61**, 104; R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1966, **88**, 650.

¹³ J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339; J. L. Franklin, *J. Chem. Phys.*, 1953, **21**, 2029; M. Szwarc, *Proc. Roy. Soc.*, 1951, **A207**, 5.

¹⁴ P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, 1962, 1360.

¹⁵ R. Criegee, *Annalen*, 1930, **481**, 263.

salt (XXI). In view of the thermal instability of malonic acid relative to acetic acid, we tentatively suggest the following mechanism in which the lead(IV) salt (XXI) readily undergoes thermal decomposition with loss of carbon dioxide resulting in the diradical species (XXII) from which, *via* intermediate (XXIII), 9,10-dihydrophenanthrene-9-carboxylic acid would readily form.



This acid would, on lead tetra-acetate oxidation, afford the 9,10-dihydrophenanthr-9-yl radical (XXV) from which the isolated phenanthrene (XIX) and 9,10-dihydrophenanthrene (XVIII) are potential products.

Fieser^{2b} used malonic acid as a promoter for the lead tetra-acetate oxidation of aromatic nitro-compounds. It is likely that in this reaction ionic interchange between malonic acid and lead tetra-acetate occurs to give the lead(IV) species $\text{CH}_2(\text{CO}_2)_2\text{Pb}(\text{OAc})_2$, which will have thermal stability below that of lead tetra-acetate. Thus radicals will be readily provided to initiate any radical-chain decomposition of lead tetra-acetate. The reaction time for the lead tetra-acetate oxidation of *o*-biphenylmethylmalonic acid was short (1 hr.) thus providing support for this suggestion.

Our results, in addition to providing additional examples of radical cyclisation, draw attention to the high yields of esters associated with acids containing the carboxy-group attached to a benzyl-type group. We suggest that for acids of this type, routes to ester formation, other than that described by equations (1) and (2), are likely.

EXPERIMENTAL

The n.m.r. spectra were determined using a Perkin-Elmer R.10 instrument operating at 60 Mc./sec., and the i.r. spectra using a Perkin-Elmer 227 grating i.r. spectrometer. Qualitative g.l.c. analysis was carried out using a Pye Argon Chromatograph and the following 4 ft. columns:

¹⁶ A. I. Vogel, 'Textbook of Practical Organic Chemistry,' Longmans, London, 1948, p. 461.

¹⁷ J. W. Cook, G. J. Dickson, J. Jack, J. D. Loudon, J. McKeown, J. Macmillan, and W. F. Williamson, *J. Chem. Soc.*, 1950, 139.

A, 10% Apiezon L (APL); B, 5% APL; quantitative analytical g.l.c. using a Griffin D6 Density Balance Chromatograph with nitrogen carrier gas and the following 6 ft columns: C, 5% APL; D, 10% APL. Celite (80–100 mesh) was used as inert support. For preparative g.l.c. a Wilkens Autoprep 700 was used employing hydrogen as carrier gas and a 20 ft \times 3/8 in. column of 30% SE 30 on 40/60 Chromosorb W. 'Woelm' neutral alumina (activity grade 1) was used for column chromatography, and 'Merck' Kieselgel G for thick-layer chromatography. The light petroleum used had b.p. 60–80°.

Preparation of Acids.—Phenylacetic acid (IV) (Hopkin and Williams), m.p. 76° from light petroleum; 3-phenylpropionic acid (XIII),¹⁶ m.p. 48.5°; 3-(*o*-biphenyl)propionic acid (XVI),¹⁷ m.p. 111.5–113°.

o-Biphenylacetic Acid (VIII).—2-Methylbiphenyl¹⁸ (16.4 g.) was dissolved in carbon tetrachloride (100 ml.) and a crystal of benzoyl peroxide was added followed by the portionwise addition of *N*-bromosuccinimide (17.4 g.) during 0.5 hr. The mixture was boiled under reflux for 1.5 hr., cooled, and the product succinimide was filtered off. Solvent was evaporated from the filtrate, and the residue was distilled to afford 2-bromomethylbiphenyl as a pale yellow oil (16.9 g.), b.p. 90°/0.04 mm. (lit.,¹⁹ b.p. 166°/12 mm.). The 2-bromomethylbiphenyl (14 g.) was added to a stirred solution of sodium cyanide (2.8 g.) in dimethyl sulphoxide (DMSO) (50 ml.). After warming at 50° for 6 hr., the mixture was diluted with water (300 ml.), and extracted with benzene (3 \times 50 ml.). The benzene extracts were washed with water (3 \times 100 ml.) to remove any DMSO, dried (MgSO_4), and distilled to yield *o*-biphenylacetonitrile as a colourless oil (11 g.), b.p. 146°/1.0 mm. (lit.,¹⁹ b.p. 182°/12 mm.). The *o*-biphenylacetonitrile (10 g.) was boiled under reflux with a mixture of concentrated hydrochloric acid (100 ml.) and glacial acetic acid (5 ml.) for 24 hr.¹⁹ The mixture was cooled and extracted with ether (3 \times 50 ml.); the ether was then extracted with *N*-sodium hydroxide solution (3 \times 50 ml.). The aqueous alkaline extract was acidified and the *o*-biphenylacetic acid (VIII) was filtered off and washed with water, dried *in vacuo*, and recrystallised from benzene–light petroleum (6.5 g.), m.p. 114° (lit.,^{18,19} m.p. 113–114°, lit.,²⁰ m.p. 116°).

3-(*o*-Methoxybiphenyl)propionic Acid (XVII). A solution of *o*-anisylmagnesium bromide [prepared from *o*-bromoanisole (90 g.), ether (400 ml.), and magnesium (11.6 g.)] was added slowly, with stirring, to a solution of 2-methylcyclohexanone (53.5 g.) in ether (200 ml.). The mixture was heated for 1 hr. to complete reaction; after being cooled, the Grignard complex was decomposed by the addition of dilute hydrochloric acid (100 ml.). The ether layer was separated, washed with water (3 \times 100 ml.) and dried (MgSO_4). The crude 1-(*o*-anisyl)-2-methylcyclohexanol obtained on evaporation of the ether (OH absorption at 3500 cm^{-1} in i.r., no carbonyl absorption) was boiled under reflux with 90% formic acid (100 ml.) for 2 hr. After evaporation of the formic acid and water, the residue (C=C absorption in i.r. at 1600 and 1570 cm^{-1}) was dissolved in ether (250 ml.), and the solution was washed with saturated sodium hydrogen carbonate solution (3 \times 50 ml.), water (3 \times 100 ml.), and finally dried (MgSO_4). The crude oil, presumably a mixture, 1-(*o*-anisyl)-2-methylcyclohex-1

¹⁸ D. G. Ott and G. G. Smith, *J. Amer. Chem. Soc.*, 1955, 77, 2325.

¹⁹ J. von Braun and G. Manz, *Annalen*, 1929, 468, 258.

²⁰ A. Schönberg and F. L. Warren, *J. Chem. Soc.*, 1939, 1838.

(and -6)-ene was purified by distillation b.p. 89°/0.3 mm. (76 g.), and intimately mixed with sulphur (25 g.) and heated at 210° for ca. 5 hr. until hydrogen sulphide evolution ceased. The resultant orange product was cooled, dissolved in light petroleum (20 ml.), and chromatographed on an alumina column (2 ft. × 0.5 in.) using light petroleum as eluant. The purified product, after treatment with animal charcoal was distilled to afford 2-methoxy-2'-methylbiphenyl (50 g.), b.p. 90°/0.15 mm., m.p. 37.5—38° from light petroleum (Found: C, 84.45; H, 6.9. C₁₄H₁₄O requires C, 84.8; H, 7.1%). A solution of 2-methoxy-2'-methylbiphenyl (10 g.) in carbon tetrachloride (100 ml.) containing benzoyl peroxide (10 mg.) was warmed on an oil-bath at 75°, and *N*-bromosuccinimide (10.4 g.) was added, portionwise, during 0.5 hr.; the heat of reaction was sufficient to maintain the solution at reflux. On completion of the addition, the mixture was warmed at 80° for 2 hr., cooled, and the succinimide was filtered off. Evaporation of solvent and distillation of product (with rejection of the first fraction boiling up to 90°/0.01 mm. containing unchanged 2-methoxy-2'-methylbiphenyl) afforded 2'-bromomethyl-2-methoxybiphenyl as a pale yellow viscous oil (11.4 g.), b.p. 110°/0.01 mm., 130°/0.15 mm., n_D^{19} 1.6223, m.p. 67° (from light petroleum) (Found: C, 60.7; H, 4.8; Br, 28.6. C₁₄H₁₃BrO requires C, 60.7; H, 4.7; Br, 28.8%). The 2'-bromomethyl-2-methoxybiphenyl (4.3 g.) was then slowly added to a stirred solution obtained by dissolving sodium ethoxide (1.3 g.) in diethyl carbonate (50 ml.) and diethyl malonate (2.71 g.). The resulting mixture was then heated at 110° for 12 hr. After cooling, water (20 ml.) and ether (100 ml.) were added, and the ether layer was separated and dried (MgSO₄). Removal of solvents and distillation of residue gave diethyl *o*-(*o*-methoxybiphenyl)methylmalonate (4.63 g.), b.p. 180°/0.15 mm., 140°/0.015 mm., m.p. 62° (from light petroleum) (Found: C, 71.1; H, 7.0. C₂₁H₂₄O₅ requires C, 70.75; H, 6.8%). The diethyl *o*-(*o*-methoxybiphenyl)methylmalonate (4 g.) was added to a solution of potassium hydroxide (2 g.) in water (10 ml.) and ethanol (25 ml.), and the mixture was heated under reflux for 6 hr. After removal of the ethanol, acidification precipitated a crude acid, which was purified by treatment with animal charcoal in boiling benzene under reflux. Addition of light petroleum to a concentrated benzene solution gave *o*-(*o*-methoxybiphenyl)methylmalonic acid as white crystals (2.9 g.), m.p. 143—143.5°. The *o*-(*o*-methoxybiphenyl)methylmalonic acid (1 g.) was heated at 160° under gentle vacuum (ca. 200 mm.) for 1 hr., until carbon dioxide evolution had ceased. The resultant oil solidified and was crystallised from light petroleum to yield 3-*o*-(*o*-methoxybiphenyl)propionic acid (XVII) (0.6 g.) as white crystals, m.p. 126—126.5° (Found: C, 74.8; H, 6.55. C₁₆H₁₆O₃ requires C, 75.0; H, 6.3%).

o-Biphenylmethylmalonic Acid (XX).—2-Bromomethylbiphenyl (7 g.) was added to a hot (80°) solution of diethyl sodiomalonate (5.7 g.) in diethyl carbonate (25 ml.), to form ethyl *o*-biphenylmethylmalonate. Bunyan and Hey¹⁴ report that this ester may be hydrolysed and the resulting acid decarboxylated by boiling at reflux with aqueous alcoholic sodium hydroxide solution. In our hands the hydrolysis of the ester in this way did not yield 3-(*o*-biphenyl)propionic acid (XVI), but rather *o*-biphenylmethylmalonic acid (XX),¹⁷ m.p. 126—127° from benzene–light petroleum (lit.,¹⁷ m.p. 125.5—126.5°).

Lead Tetra-acetate Oxidation of Acids.—This was carried out according to the general procedure described in Part I.⁶

The quantities of reactants and yields of products are recorded in the Table. Compounds were identified by qualitative g.l.c. analysis on column A [for esters, bibenzyl (II), diphenylmethane (III), and related compounds] and column B [for phenanthrene (XIX), 9,10-dihydrophenanthrene (XVIII), and related high molecular weight hydrocarbons], by a comparison of g.l.c. retention times with those of authentic specimens. Esters, bibenzyl (II), and diphenylmethane (III) were isolated by preparative-gas chromatography with temperature programmed runs between 150° and 250°. Phenanthrene (XIX) and 9,10-dihydrophenanthrene (XVIII) were best isolated by thick-layer chromatography using light petroleum as eluant. The yields of esters, bibenzyl (II), and diphenylmethane (III) were estimated by quantitative g.l.c. analysis at 200° on column D; for phenanthrene (XIX) and 9,10-dihydrophenanthrene (XVIII) column C was employed. The following notes record details of the oxidation of the various acids not given in the Table and in the general summary above.

Phenylacetic Acid (IV).—Fluorene was used as marker for quantitative g.l.c. analysis. When an oxidation was carried out in which phenylacetic acid (IV) was replaced by bibenzyl (II), little of the hydrocarbon was consumed during one week.

o-Biphenylacetic Acid (VIII). The two main products were isolated by preparative g.l.c. The product of higher retention time, a colourless oil, was identified by n.m.r. (absorptions at τ 2.40, aromatics; 4.76, ArCH₂OCO—; 7.98, OCOCH₃) and i.r. (ester carbonyl at 1750 cm.⁻¹) as *o*-biphenylmethyl acetate (X), b.p. 120°/0.1 mm., n_D^{24} 1.5712 (lit.,²¹ oil, b.p. 182°/20 mm.) (Found: C, 79.7; H, 6.3. Calc. for C₁₅H₁₄O₂: C, 79.6; H, 6.25%). The product of lower retention time was collected as a yellow oil and purified by molecular distillation to give a colourless oil which turned yellow after a few hours at room temperature. The n.m.r. spectrum of the crude product showed absorptions at τ 2.6—2.8, aromatic; 5.50, singlet, ArCH₂O—? in the ratio 4:1 (Found: C, 78.9; H, 5.55. C₁₃H₁₀O₂ requires C, 78.75; H, 5.1). This product may be the cyclic peroxide (XI). The presence of fluorene (IX), 2,2'-diphenylbibenzyl, and 2-benzylbiphenyl could not be identified by either g.l.c. or t.l.c. 2-Methylbiphenyl was a trace product. Naphthalene was used as marker for quantitative g.l.c. analysis.

3-Phenylpropionic Acid (XIII).—Qualitative g.l.c. indicated two volatile trace products in addition to the major product bibenzyl (II). 1,4-Diphenylbutane and dihydrocoumarin (XIV) could not be detected. Biphenyl was used as marker for quantitative g.l.c. analysis.

3-(o-Biphenyl)propionic Acid (XVI).—Bibenzyl (II) was used as marker for quantitative g.l.c. analysis.

3-o-(o-Methoxybiphenyl)propionic Acid (XVII).—Qualitative g.l.c. analysis indicated two other products in addition to 9,10-dihydrophenanthrene (XVIII). The scale of our reaction was insufficient for adequate separation and isolation of these other products.

o-Biphenylmethylmalonic Acid (XX).—Bicumyl was used as marker for quantitative g.l.c. analysis.

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²¹ R. Fanto, *Monatsh.*, 1898, 19, 584.