961. *The Photochemical Decomposition of Some Aryl Esters*

By W. M. HORSPOOL and P. L. PAUSON

The behaviour of several phenyl and *p*-t-butylphenyl esters is studied. Of these the formates are shown to give the best yields of free phenol on irradiation. Some evidence for intermediate formation of free radicals is presented.

SEVERAL recent publications [1-3] have dealt with the decomposition of phenyl and substituted phenyl esters by light. One of these [2a] was primarily concerned with the suitability of certain esters as photolytically removable protective groups. In the others, the emphasis was on the formation of C-acyl phenols and the reaction has therefore been described as the "photochemical Fries rearrangement." The simultaneous formation of free phenols was however noted. Our interest turned to the latter products in view of the possibility that their formation might occur *via* the corresponding phenoxy-radicals. If so, the process would provide a route to such radicals not involving phenol oxidation. We have therefore studied a number of such photolytic reactions with a view to finding conditions for the formation of the maximum amount of free phenol rather than rearrangement products. In this respect the present results supplement those of Barton *et al.*[2a] Whereas these authors devoted their attention chiefly to naphthyl esters of relatively complex acids, our work deals with the carbonates, formates, and oxalates of phenol and *p*-t-butylphenol. The experiments described below suggest that the formates are of comparable efficiency as phenol producers with the fluorene-9-carboxylates.[2a]

<div align="center">EXPERIMENTAL</div>

Starting Materials.—Aryl oxalates were prepared by the method of Adickes *et al.*[4] Diphenyl oxalate so obtained (15%) had m. p. 142° (lit.,[4] m. p. 134°), $\nu_{max.}$ (CCl$_4$) 1788, 1764 cm.$^{-1}$ (C=O).

[1] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 1960, 217; *J.*, 1963, 1781.
[2] (a) D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *Tetrahedron Letters*, 1962, 1055; (b) H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293.
[3] C. H. Kuo *et al.*, *Chem. and Ind.*, 1960, 1627.
[4] F. Adickes, W. Brunnert, and O. Lücker, *J. prakt. Chem.*, 1931, **130**, 163 and 174.

Di-p-*t*-*butylphenyl oxalate* (13·5% yield) formed prisms (from light petroleum), m. p. 152·5—154·5° (Found: C, 74·1; H, 7·4. $C_{22}H_{26}O_4$ requires C, 74·5; H, 7·4%), $\nu_{max.}$ (CCl$_4$) 1789, 1767 cm.$^{-1}$ (C=O). Several formates were obtained by a slight modification of the same method [4] as follows: The phenol (0·5 mole), phosphorus oxychloride (0·75 mole), formic acid (2·5 mole; 100%), and aluminium chloride (0·045 mole) were heated on a water-bath at 60° for 10 hr. The mixture was cooled and extracted with ether (250 ml.). The extract was washed twice with water, dried (Na$_2$SO$_4$), filtered, and evaporated. The residue was distilled (12—15 mm.) and the distillate chromatographed on silica gel (30 g. per g. of formate). The desired formate was eluted with light petroleum–benzene (3 : 1). Redistillation gave the following as colourless oils: Phenyl formate (24·9%), b. p. 74—76°/12 mm. (lit.,[4] b. p. 72·5—73·5°/10 mm.), $\nu_{max.}$ (liq. film) 1762, 1742 cm.$^{-1}$ (C=O); p-*t*-*butylphenyl formate* (36·0%), b. p. 128°/20 mm., n_D^{22} 1·5011 (Found: C, 74·0; H, 8·3. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%), $\nu_{max.}$ (CCl$_4$) 1786, 1760 cm.$^{-1}$ (C=O); 2,6-*xylyl formate* (58·5%), b. p. 91°/12—15 mm., n_D^{20} 1·5065 (Found: C, 72·3; H, 7·0. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%), $\nu_{max.}$ (liq. film) 1770, 1740 cm.$^{-1}$ (C=O); p-*chlorophenyl formate* (29·6%), b. p. 87—88°/12 mm., n_D^{24} 1·5298 (Found: C, 54·0; H, 3·2; Cl, 23·1. $C_7H_5ClO_2$ requires C, 53·5; H, 3·2; Cl, 22·7%), $\nu_{max.}$ (liq. film) 1773, 1754 cm.$^{-1}$ (C=O); 2-*naphthyl formate* (21·0%), b. p. 148°/12 mm., colourless needles, m. p. 23—24° (Found: C, 77·4; H, 4·7. $C_{11}H_8O_2$ requires C, 76·8; H, 4·7%), $\nu_{max.}$ (liq. film) 1767, 1742 cm.$^{-1}$ (C=O).

Attempted Synthesis of 2-Allyl-4-t-butylphenyl Formate.—(*a*) 2-Allyl-4-t-butylphenol (15·5 g.; 0·08 mole; b. p. 78°/0·3 mm.) (lit.,[5] b. p. 125—126°/5 mm.) phosphorus oxychloride (17·6 ml.; 30 g.; 0·2 mole), formic acid (22 g.; 18 ml.; 0·5 mole), and aluminium chloride (0·6 g.) were heated on an oil-bath for 8 hr. at 70°. The resulting black material was dissolved in ether and washed with cold water (2 × 50 ml.). After the ethereal solution had been dried over anhydrous sodium sulphate and evaporated the residue was chromatographed on silica gel. Light petroleum–benzene (3 : 1) eluted 4-*t*-*butyl*-2-(2′-*chloropropyl*)*phenyl formate* (5·8 g.; 28%), b. p. 99—101°/0·15 mm., n_D 1·5111 (Found: C, 66·9; H, 8·0; Cl, 14·0. $C_{14}H_{19}ClO_2$ requires C, 66·0; H, 7·5; Cl, 14·0%), $\nu_{max.}$ (liq. film) 1770, 1745 cm.$^{-1}$ (C=O). Its n.m.r. spectrum showed peaks at 1·80 τ (OCHO); 2·75 and 2·94 τ (3 aromatic protons); 5·82, 6·96, and 7·12 τ (side chain) and 8·70 τ (Bu^t).

(*b*) 2-Allyl-4-t-butylphenol (9·5 g.; 0·05 mole) and formic acid (100%; 28 g.; 23 ml.; 0·5 mole) were refluxed for 24 hr. After cooling, the mixture was dissolved in ether (100 ml.) and washed twice with cold water (2 × 50 ml.). The ethereal solution was dried over anhydrous sodium sulphate and distilled to remove ether. The residue was chromatographed on silica gel. Light petroleum–benzene (3 : 1) eluted 6-t-butyl-2,3-dihydro-2-methylbenzofuran (3·8 g.) b. p. 62—64°/0·2 mm. (lit.,[5] b. p. 106—107°/2 mm.). Benzene–ether (9 : 1) eluted unchanged 2-allyl-4-t-butylphenol (4·3 g.).

2-Allyl-4-t-butylphenyl Formate.—2-Allyl-4-t-butylphenol (19·0 g.; 0·1 mole), formic acid (100%; 4·6 g.; 0·1 mole), and dicyclohexylcarbodi-imide (20·6 g.; 0·1 mole) were allowed to react in dry tetrahydrofuran (500 ml.) according to the method of Buzas *et al.*[6] The mixture was maintained at 0° during the addition of the carbodi-imide and then stored in a refrigerator for 24 hr. During this time occasional evolution of gas was noticed. After filtration, to remove dicyclohexylurea, the solvent was distilled off and the residue was chromatographed on a long column (4 ft. × ¾ in.) of silica gel. Light petroleum–benzene (3 : 1) eluted 6-t-butyl-2,3-dihydro-2-methylbenzofuran (4·9 g.) identical with the sample obtained from the preceding experiment. Further elution with the same solvent afforded 2-*allyl-4-t-butylphenyl formate* (7·4 g.; 34·0%), b. p. 111°/12 mm., n_D^{24} 1·5079 (Found: C, 78·0; H, 8·8. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%), $\nu_{max.}$ (liq. film) 1770, 1748 cm.$^{-1}$ (C=O).

p-*Tolyl Formate.*—This was synthesised similarly by the reaction of *p*-cresol (13·6 g.; 0·1 mole), and dicyclohexylcarbodi-imide (20·6 g., 0·1 mole) in dry tetrahydrofuran (250 ml.) for 24 hr. in a refrigerator. Chromatography on silica gel yielded p-*tolyl formate* on elution with light petroleum–benzene (3 : 1) (4·7 g., 34·5%), b. p. 74—75°/12 mm., n_D^{24} 1·5070 (Found: C, 70·6; H, 5·9. $C_8H_8O_2$ requires C, 70·5; H, 5·9%), $\nu_{max.}$ (liq. film) 1786, 1755 cm.$^{-1}$ (C=O).

Irradiation Experiments.—The aryl ester was dissolved in 650 ml. of solvent and irradiated with a 500w medium-pressure mercury arc lamp (Hanovia 509/12) contained in a water-cooled quartz tube in the centre of the apparatus. An atmosphere of " white spot " nitrogen, used without further purification, was maintained over the solution from which samples were removed

[5] A. B. Sen and R. P. Rastogi, *J. Indian Chem. Soc.*, 1953, **30**, 355 (*Chem. Abs.*, 1954, **48**, 10,649).
[6] A. Buzas, C. Egnell, and P. Freon, *Compt. rend.*, 1962, **255**, 945; 1963, **256**, 1804.

Reaction ArOCOR $\xrightarrow{hv}$ ArOH + o-RCOArOH + polymer

Example	ArOCOR Ar	ArOCOR R	Quantity g.	Quantity mole	Solvent	Time hr.	Conversion[a] %	ArOH g.	ArOH %[b]	o-RCOArOH g.	o-RCOArOH %[b]	"Polymer" g.	"Polymer" %[b]	Other
1	Ph	Ph	10.0	0.05	Ethanol	70	38	0.45	4.5	1.77	18			p-PhCO·C$_6$H$_4$OH 1.60 g. (16%) (o-HO·C$_6$H$_4$)$_2$CO 0.41 g. (4%)
2	Ph	OPh	10.0	0.046	Ethanol	150	42	—	—	—	—	2.0	20	o-HO·C$_6$H$_4$·CO·C$_6$H$_4$OH-p 1.1 g. (11%)
3	Ph	o-C$_6$H$_4$OH	10.7	0.05	Ethanol	76	52	0.12	1	2.0	19	0.9	8	o-HO·C$_6$H$_4$·CO·C$_6$H$_4$OH-p 2.32 g. (22%)
4	p-Bu^{t}C$_6$H$_4$	p-O·C$_6$H$_4$Bu^t	8.0	0.024	Ethanol	24	85	1.8	22.5	0.2	2[c]	2.1	26	(A)[a,d] 2.1 g. (26%) (B)[e] trace
5	p-Bu^{t}C$_6$H$_4$	p-O·C$_6$H$_4$Bu^t	8.0	0.024	Benzene	24	81	2	27	—	—	1.2	15	(A)[a] 2.9 g. (36%)
6	Ph	CO$_2$Ph	3.63	0.015	Ethanol	32	92	0.78	23.5	—	—	1.8	54	—
7	p-Bu^{t}C$_6$H$_4$	p-CO$_2$C$_6$H$_4$Bu^t	4.0	0.012	Ethanol	24	81.5	1.37	40	—	—	1.5	37.5	—
8	Ph	H	6.1	0.05	Ethanol	20	100	2.13	49	—	—	3.0	50	—
9	p-Bu^{t}C$_6$H$_4$	H	8.9	0.05	Ethanol	12	98.5	6.02	80	—	—	1.05	12	[2,5-(HO)Bu^{t}C$_6$H$_3$]$_2$ 0.05 g. (0.5%)
10	p-Bu^{t}C$_6$H$_4$	H	8.9	0.05	Benzene	39	75	4.16	55	0.6	7[f]	0.76	8.5	
11	p-Bu^{t}C$_6$H$_4$	CH$_3$[g]	4.8	0.025	Ethanol	31	100	1.3	34.5	1.41	34[h]	1.11	23	

[a] 100 minus percentage ArOCOR recovered. [b] Based on ArOCOR irradiated. [c] Chromatographed with unchanged 2,2'-di-t-butylphenyl carbonate. After hydrolysis (50 ml. 1N-KOH in 1 : 1 ethanol–water, 2 hr.) of this mixture the hydrogen carbonate-soluble fraction afforded 5-t-butylsalicylic acid (0.11 g.), m. p. 154—155° (from ethanol; lit.[7] m. p. 151°) (Found: C, 67.5; H, 7.6. Calc. for C$_{11}$H$_{14}$O$_3$: C, 68.0; H, 7.2%). [d] 5,5'-Di-t-butyl-2,2'-dihydroxybenzophenone eluted by light petroleum–benzene (3 : 1) formed yellow needles, m. p. 104—106°, from aqueous ethanol (Found: C, 77.4; H, 8.0%). It showed $\nu_{max.}$ (CCl$_4$) at 1626 cm.$^{-1}$ (C=O) and gave a 2,4-dinitrophenylhydrazone, m. p. 253—255° from ethanol (Found: C, 63.5; H, 6.6; N, 10.7. C$_{27}$H$_{30}$N$_4$O$_6$ requires C, 64.0; H, 5.9; N, 11.1%). [e] 5,5'-Di-t-butyl-2,2'-dihydroxybiphenyl, obtained as colourless needles, m. p. 210—212° from 2,2,4-trimethylpentane (lit.[8] m. p. 207—208°) (Found: C, 80.4; H, 8.8. Calc. for C$_{20}$H$_{26}$O$_2$: C, 80.5; H, 8.7%), $\nu_{max.}$ (KCl disc) 3175 cm.$^{-1}$ (OH). [f] Lit.[9] b. p. 138—140°/12 mm. (Found: C, 74.7; H, 8.4. C$_{11}$H$_{14}$O$_2$ requires C, 74.1; H, 7.9%), $\nu_{max.}$ (liquid film) 1662 cm.$^{-1}$ (C=O). Its 2,4-dinitrophenylhydrazone has m. p. 267—270° (decomp.) (Found: N, 15.4. C$_{17}$H$_{18}$N$_4$O$_5$ requires N, 15.6%). [g] B. p. 244—246°/760 mm. (lit.[9,10] b. p. 165°/5 mm.). [h] B. p. 72—73°/0.15 mm. (lit.[10] b. p. 130°/12 mm.), $\nu_{max.}$ (liq. film) 1646 cm.$^{-1}$ (C=O); 2,4-dinitrophenylhydrazone, m. p. 173—174° (lit.[10] m. p. 170°).

[7] H. Meyer and K. Bernhauer, *Monatsh.*, 1929, **53/54**, 721.
[8] W. W. Kaeding, *J. Org. Chem.*, 1963, **28**, 1063.
[9] T. A. Henry and T. M. Sharp, *J.*, 1926, 2432.
[10] A. B. Sen and T. N. Kakaji, *J. Indian Chem. Soc.*, 1952, **29**, 950 (*Chem. Abs.*, 1954, **48**, 2606).

periodically to follow the disappearance of the ester-carbonyl infrared absorption. After removal of the solvent by distillation, the residue was chromatographed on silica gel. Light petroleum–benzene (3 : 1) eluted the unchanged esters, followed by the *ortho*-rearrangement products. Benzene eluted the phenols, ArOH, and then the *para*-rearrangement products and benzene–ether (1 : 1) eluted intractable gums of higher molecular weight referred to as " polymers " in the Table.

The gas evolved during the irradiation of *p*-t-butylphenyl formate in ethanol (1·75 l., equivalent to 1·5 mole per mole of formate) was trapped over water and shown by its infrared spectrum to contain carbon monoxide ($\nu_{max.}$ 2198, 2137 cm.$^{-1}$). The gas from *p*-t-butylphenyl acetate (234 ml.) was a mixture of carbon monoxide and a gaseous hydrocarbon, presumably methane ($\nu_{max.}$ 3012, 2959, and 2899 cm.$^{-1}$). The solvent from both these irradiations when distilled into Brady's reagent gave samples (0·4 and 0·24 g., respectively) of acetaldehyde 2,4-dinitrophenylhydrazone.

<div align="center">DISCUSSION</div>

Irradiation of the benzoate (example 1) gives chiefly rearranged products as has been found independently by Anderson and Reese,[1] with whose results our findings agree (minor differences being attributable to different reaction conditions). Rearrangement was again the main effect of irradiation on both the unsubstituted (example 2) and the di-t-butyl substituted (example 4) phenyl carbonates. That the formation of dihydroxybenzophenones from these carbonates involves two successive rearrangement steps with the corresponding phenyl salicylates as intermediates was shown in the latter case by isolation (after hydrolysis) of a small quantity of 5-t-butylsalicylic acid. It was further shown in the unsubstituted series (example 3) that phenyl salicylate rearranges more rapidly than the carbonate to the same two dihydroxybenzophenones.

Much better conversion into phenol was achieved with the oxalates and formates. The oxalates did not give rearrangement products, but gave considerable amounts of intractable (polymeric) material. The formates gave by far the best yields of phenols and the irradiation of *p*-t-butylphenyl formate in ethanol proved outstanding in this respect (example 9). Even in benzene the irradiation of this formate (example 10) gave only a small yield of rearrangement product, 5-t-butylsalicylaldehyde. The improved yield of phenol when ethanol is the solvent is consistent with hydrogen abstraction from the solvent by intermediate radicals (ArO· and/or ·CHO). To support this postulate, formation of acetaldehyde from the solvent was demonstrated in two cases (examples 9 and 11). It is less clear whether all the radicals become genuinely free or whether a significant proportion of the products are due to a cage effect (cf. ref. 2*b*) resulting in further interactions between the initially formed radicals (steps B, C, and D), or even purely internal rearrangements (steps E and F, cf. ref. 1):
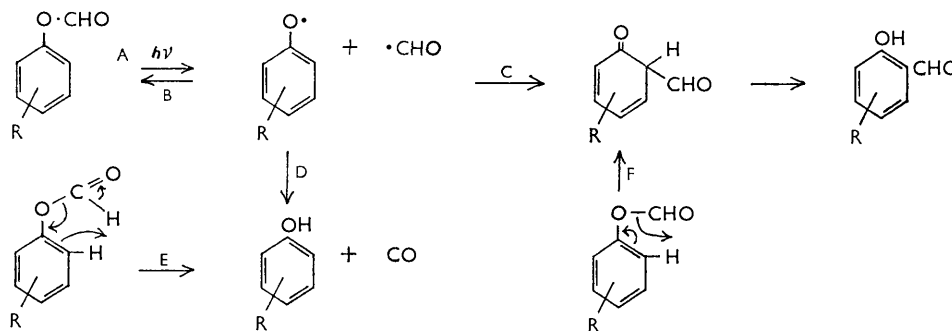
The formation of phenol when the reaction is conducted in benzene is most readily explained by step D. On the other hand, no analogous step exists for phenol formation from the other esters, especially the oxalates. Formation of at least some free radicals is also necessary

to account for the formation of the biphenyl, 2,2'-dihydroxy-5,5'-di-t-butylbiphenyl (example 9) and of the hydrocarbon gas (presumably methane) derived from the acyl group of *p*-t-butylphenyl acetate (example 11).

Several new formates and a new oxalate were prepared during this work. Most of these were obtained, albeit in moderate or poor yields, by an established procedure [4] involving condensation of the phenol and acid in the presence of phosphorus oxychloride. With 2-allylphenol however, simultaneous addition of hydrogen chloride and partial cyclisation occurred. The desired formate was therefore prepared by adaptation of the carbodi-imide method of esterification.[6]