

440. Benzoyloxylation, Halogenation, and Phenylation of Aromatic Compounds by Silver Bromide Dibenzoate and Silver Iodide Dibenzoate.

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The complexes $(\text{Ph}\cdot\text{CO}_2)_2\text{AgHal}$ which are formed by the reaction between silver benzoate and bromine or iodine can react with aromatic compounds in the three ways indicated in the title. Evidence is presented that the phenylation is a homolytic process which involves free phenyl radicals derived from thermal decomposition of the complexes. Of the two reagents, silver iodide dibenzoate tends to give the higher proportion of phenylation products. The benzoyloxylation and the halogenation both have the character of electrophilic substitutions. The nucleophilic character of the substrate appears largely to determine the proportions in which the three reactions occur. The relative velocities of benzoyloxylation and bromination are reversed on passing from chlorobenzene to anisole. The reason for this is discussed with reference to the possibility of transition-state resonance involving the entering substituent.

REACTIONS between silver carboxylates and halogens have often been used to prepare organic halides, particularly alkyl halides.^{1,2} The overall equation may be written: $\text{R}\cdot\text{CO}_2\text{Ag} + \text{X}_2 \longrightarrow \text{RX} + \text{CO}_2 + \text{AgX}$ (X = halogen). It has been suggested that RX

¹ Kleinberg, *Chem. Rev.*, 1947, **40**, 381.

² Johnson, *Ann. Reports*, 1949, **46**, 154.

is formed by the decarboxylation of an intermediate acyl hypohalite, $R\cdot CO_2X$.^{3,4} However, Simonini⁵ showed that the reaction of a silver carboxylate with *one* atomic equivalent of a halogen gives a complex of the general formula $(R\cdot CO_2)_2AgX$, and this has been confirmed by subsequent workers.^{6,7} Prévost⁸ found that these complexes—the silver halide dicarboxylates—can oxidise olefinic compounds to give glycol esters, but that a substitution occurs with acetylenes: ⁹ *e.g.*, $(Ph\cdot CO_2)_2AgI + R\cdot C\equiv CH \longrightarrow R\cdot C\equiv CI + Ph\cdot CO_2Ag + Ph\cdot CO_2H$. Reactions between silver halide dicarboxylates and aromatic compounds have received little attention. Birckenbach and Meisenheimer¹⁰ observed that aryl halides and benzoates were produced when silver benzoate was treated with two atomic equivalents of a halogen in the presence of certain aromatic compounds; but the active reagents under their conditions were probably not silver halide dibenzoates. Prévost and Wiemann⁹ obtained phenyl benzoate from an attempted preparation of silver bromide dibenzoate in benzene, and they thought it likely that the aromatic solvent took part in the reaction.

The present work is an examination of the reactions between two silver halide dibenzoates and five aromatic compounds of differing nucleophilic character. A preliminary account has already been presented by one of us.¹¹

EXPERIMENTAL

Preparation and Purification of Materials.—Silver benzoate was prepared from equimolecular proportions of sodium benzoate and silver nitrate. "AnalaR" bromine and iodine were used. Benzene and *n*-pentane were purified as described by Bryce-Smith and Turner.¹² Nitrobenzene and chlorobenzene were purified as described by Augood, Hey, and Williams.¹³ Anisole was shaken with aqueous sodium hydroxide, washed, dried, and distilled through a 180-cm. column of Fenske helices, a middle fraction boiling over a range of 0.1° being used. *tert.*-Butylbenzene was prepared from *tert.*-butyl chloride and benzene by the Friedel-Crafts method, and was shaken repeatedly with portions of concentrated sulphuric acid, washed, dried, and fractionated as for anisole. All materials and apparatus were thoroughly dried before use. Reactions were performed under nitrogen.

General Procedure for the Preparation and Decomposition of the Complexes.—(i) *Silver bromide dibenzoate.* Two methods were used to prepare this reagent. In the cases of the less reactive solvents, nitrobenzene, chlorobenzene and benzene, 1 atomic equivalent of bromine was added dropwise to a well-stirred suspension of silver benzoate in the solvent at room temperature, residues being washed in with a little additional solvent. The bromine reacted almost immediately under these conditions. In the cases of *tert.*-butylbenzene and anisole, the possibility of direct bromination of the solvent was avoided by preparing the reagent separately in the minimum amount of *n*-pentane before its addition to the aromatic compound. The mixture was kept at the required temperature until a sample of the stirred suspension showed no oxidising power with aqueous potassium iodide. The silver salts were removed by filtration and treated with dilute ammonia solution to extract silver benzoate, which was estimated as silver iodide. Free benzoic acid was extracted from the organic solution with saturated aqueous sodium hydrogen carbonate solution (5 × 100 ml.). The other organic products were separated and identified by methods appropriate to each.

(ii) *Silver iodide dibenzoate.* A procedure similar to that above was employed, finely powdered iodine being added from a gas-tight hopper. Since iodine is unreactive towards all the solvents which were used, the preliminary preparation of the complex in *n*-pentane was unnecessary.

The yields of products not mentioned in experiments (a)—(j) below are listed in Tables 1 and 2.

³ Birckenbach, Goubeau, and Berninger, *Ber.*, 1932, **65**, 1339.

⁴ Bockemüller and Hofmann, *Annalen*, 1935, **519**, 165.

⁵ Simonini, *Monatsh.*, 1893, **14**, 81.

⁶ Wieland and Fischer, *Annalen*, 1926, **446**, 49.

⁷ Crawford and Simonds, *J. Amer. Chem. Soc.*, 1955, **77**, 2605.

⁸ Prévost, *Compt. rend.*, 1933, **196**, 1129; **197**, 1661.

⁹ Prévost and Wiemann, *ibid.*, 1937, **204**, 989.

¹⁰ Birckenbach and Meisenheimer, *Ber.*, 1936, **69**, 723.

¹¹ Bryce-Smith, *Nature*, 1953, **172**, 863.

¹² Bryce-Smith and Turner, *J.*, 1953, 861.

¹³ Augood, Hey, and Williams, *J.*, 1952, 2094.

Reactions of Silver Bromide Dibenzoate with Aromatic Compounds.—(a) *Nitrobenzene.* The complex was prepared from silver benzoate (25.88 g.) and bromine (9.018 g.) in nitrobenzene (240 ml.) and its decomposition was complete after 20 hr. at 45°. Carbon dioxide was evolved. After the removal of nitrobenzene by fractionation under reduced pressure, a yellow liquid product was obtained, having b. p. 105—140°/0.4 mm. (3.3 g.). This partly solidified in ice. Recrystallisation from ethyl alcohol, repeated four times, gave *m*-nitrophenyl benzoate (0.4 g.), m. p. 91° and mixed m. p. 92° (Found: N, 5.7. Calc. for C₁₃H₉O₂N: N, 5.75%). Control experiments showed that any of the less-soluble *para*-isomer would have been concentrated by this process. The mother-liquors from the recrystallisation were combined and the alcohol was removed under reduced pressure. The residue was heated under reflux with 10% aqueous potassium hydroxide (50 ml.) for 20 hr. Unhydrolysed material was extracted with ether. Distillation of the dried extract gave a mixture of nitrodiphenyls (0.8 g.), b. p. 115—122°/0.3 mm. (Found: N, 7.0. Calc. for C₁₂H₉O₂N: N, 7.05%).

(b) *Chlorobenzene.* The complex was prepared from silver benzoate (24.27 g.) and bromine (8.495 g.) in chlorobenzene (250 ml.), and its decomposition was complete after 40 hr. at 20°. No carbon dioxide was evolved. Chlorobenzene was removed by fractionation under reduced pressure. Distillation of the residue gave a fraction, b. p. 120—160°/1 mm. (6.1 g.), which was largely a mixture of isomeric chlorophenyl benzoates. Recrystallisation of a portion from alcohol gave *p*-chlorophenyl benzoate, m. p. and mixed m. p. 88° (Found: Cl, 15.4. Calc. for C₁₃H₉O₂Cl: Cl, 15.25%). Another portion (2.2 g.) was purified for infrared analysis (described below) by chromatography on silica gel, with mixtures of light petroleum (b. p. <40°) and methylene dichloride as eluants. 2.0 G. of colourless material were obtained after redistillation. A little brown material remained on the column. No odour of chlorodiphenyls was detected.

(c) *Benzene.* The complex was prepared from silver benzoate (22.70 g.) and bromine (8.284 g.) in benzene (200 ml.), and its decomposition was complete after 5 hr. at 20°. No carbon dioxide was evolved. Benzene was distilled off at 760 mm. The residue gave bromobenzene (0.34 g.), b. p. 45—55°/22 mm. (Found: Br, 50.3. Calc. for C₆H₅Br: Br, 50.9%), and phenyl benzoate (5.17 g.), m. p. 64—66° without recrystallisation. Recrystallisation from alcohol gave pure phenyl benzoate, m. p. and mixed m. p. 68°. No odour of diphenyl was detected.

In a control experiment, silver benzoate (12.4 g.) was stirred with benzene (100 ml.) and bromobenzene (10 g.) for 1 hr. at 80°. No silver bromide was produced.

(d) *tert.-Butylbenzene.* The complex was prepared from silver benzoate (25.46 g.) and bromine (8.897 g.) in *n*-pentane (190 ml.). *tert.*-Butylbenzene (200 ml.) was then added and the mixture was stirred at 20° for 50 hr. No carbon dioxide was evolved. The solvents were removed and the bulk of the residue was distilled over the range 40—145°/0.5 mm. This material was heated under reflux with 10% aqueous potassium hydroxide (50 ml.) for 20 hr. Extraction with ether gave a slightly impure mixture of bromo-*tert.*-butylbenzenes (0.783 g.), b. p. 100—116°/20 mm. (Found: C, 59.6; H, 6.4; Br, 33.4. Calc. for C₁₀H₁₃Br: C, 56.4; H, 6.1; Br, 37.5%). The analysis corresponding to a mixture containing 15 mol. % of *tert.*-butylbenzene as impurity is: C, 59.6; H, 6.6; Br, 33.8%. On this basis, the corrected yield of bromo-*tert.*-butylbenzenes is 0.70 g. The aqueous layer from the hydrolysis was saturated with carbon dioxide, and the phenols were extracted with ether. By recrystallisation of the toluene-*p*-sulphonates from methanol, *p*-*tert.*-butylphenyl toluene-*p*-sulphonate (0.06 g.) was obtained, with m. p. and mixed m. p. 110—111°. The aqueous layer from the hydrolysis also furnished benzoic acid (0.72 g.), from which yield the total yield of esters was calculated (Table 1). Experimental difficulties prevented any more detailed investigation of the products of this reaction. The low yields of substitution products are attributed to attack of the alkyl side-chain in a competing reaction: cf. experiment (k).

(e) *Anisole.* The reagent was prepared from silver benzoate (24.16 g.) and bromine (8.438 g.) in *n*-heptane (120 ml.). Anisole (150 ml.) was then added. The reaction was complete after 15 minutes' stirring at 20°. No carbon dioxide was evolved. After removal of the solvents the bulk of the residue distilled over the range 90—106°/17 mm. (4.58 g.). This was heated under reflux with 20% aqueous sodium hydroxide (5 ml.) for 4 hr. Extraction with ether and distillation of the extract gave *p*-bromoanisole (4.20 g.), b. p. 100—106°/17 mm., m. p. and mixed m. p. 12.5° (Found: Br, 42.4. Calc. for C₇H₇OBr: Br, 42.8%). Since the pure *para*-isomer was obtained directly by distillation in this way, the *ortho*- and the *meta*-isomer must have been absent. Benzoic acid (0.15 g.) was obtained from the aqueous layer from the hydrolysis.

(f) *Competition experiment between benzene and chlorobenzene.* The complex was prepared from silver benzoate (16.85 g.) and bromine (5.887 g.) in a mixture of benzene (44.0 g.) and chlorobenzene (276.5 g.). The mixture was stirred at 20° for 15 hr. The resulting mixture of

phenyl benzoate and isomeric chlorophenyl benzoates was purified for infrared analysis by methods similar to those described in experiment (b).

Reactions of Silver Iodide Dibenzoate with Aromatic Compounds.—(g) *Nitrobenzene.* The complex was prepared from silver benzoate (21.99 g.) and iodine (12.19 g.) in nitrobenzene (200 ml.). The mixture was stirred at 130° for 22 hr. Carbon dioxide was slowly evolved. The neutral products were worked up as in experiment (a). In the present case, recrystallisation of the mixture of nitrodiphenyls and nitrophenyl benzoates gave 4-nitrodiphenyl, m. p. and mixed m. p. 110—111°. Hydrolysis of the material obtained from the combined mother-liquors gave nitrodiphenyls (2.96 g.) (Found: C, 71.75; H, 4.6; N, 7.3. Calc. for C₁₂H₉O₂N: C, 72.35; H, 4.55; N, 7.05%), together with benzoic acid (1.6 g.).

(h) *Chlorobenzene.* The complex was prepared from silver benzoate (22.55 g.) and iodine (12.50 g.) in chlorobenzene (300 ml.). The mixture was stirred at 130° for 20 hr. Carbon dioxide was slowly evolved. The neutral product, a mixture of chlorodiphenyls and chlorophenyl benzoates (5.80 g.), was collected over the b. p. range 80—140°/0.3 mm. This mixture was heated under reflux with 10% aqueous potassium hydroxide (100 ml.) for 20 hr. Extraction with ether gave chlorodiphenyls (3.86 g.) (Found: Cl, 19.1. Calc. for C₁₂H₉Cl: Cl, 18.8%). Benzoic acid (0.95 g.) was obtained from the aqueous layer.

(i) *Benzene.* The complex was prepared from silver benzoate (22.29 g.) and iodine (12.35 g.) in benzene (350 ml.). The mixture was heated at 80° for 140 hr. Carbon dioxide was slowly evolved. The neutral material which remained after removal of most of the benzene was shaken with a little sodium thiosulphate solution to remove traces of free iodine. Distillation gave a colourless solid (3.88 g.), b. p. 70—100°/0.5 mm. This contained 1.85% of iodine, considered due to the presence of iodobenzene. Recrystallisation of a portion of the solid from alcohol gave diphenyl, m. p. and mixed m. p. 69°. Iodobenzene would have co-distilled with diphenyl under the above conditions. Hydrolysis of another portion of the solid (3.33 g.) gave benzoic acid (0.02 g.).

(j) *Anisole.* The complex was prepared from silver benzoate (19.86 g.) and iodine (11.01 g.) in anisole (250 ml.). The mixture was stirred at 100° for 5 hr. No carbon dioxide was evolved. Anisole was removed by distillation under reduced pressure, and the neutral products were heated under reflux with 20% aqueous sodium hydroxide (5 ml.) for 4 hr. Extraction with ether, followed by distillation, gave iodoanisoles (7.61 g.), b. p. 106—110°/10 mm. (Found: I, 54.3. Calc. for C₇H₇OI: I, 54.3%). A portion (6.40 g.) of this material was recrystallised from aqueous alcohol (1:4) to give *p*-iodoanisole (6.01 g.), m. p. and mixed m. p. 50°. Benzoic acid (0.08 g.) was also obtained from the hydrolysis.

(k) *isoPropylbenzene.* The complex was prepared from silver benzoate (9.2 g.) and iodine (5.1 g.) in *isopropylbenzene* (60 ml.). The mixture was heated at 150° for 2 hr. Carbon dioxide was evolved during the first 30 min. 9.2 g. (98%) of silver iodide were obtained, together with 2.6 g. of benzoic acid. The neutral products contained a little acetophenone, which was identified as the semicarbazone, m. p. and mixed m. p. 198°. No other products were identified.

Infrared Spectrographic Analysis.—A double-beam Grubb-Parsons instrument was used. The general procedure was similar to that described by Augood, Hey, and Williams.¹⁴ Nitromethane was used as a solvent.

(i) *Chlorophenyl benzoates.* The *ortho*-, *meta*-, and *para*-isomers have strong absorption peaks at 12.38, 12.80, and 13.18 μ respectively, and measurements at these wavelengths were used to determine the composition of the mixture of chlorophenyl benzoates obtained in experiment (b). A solution of known quantities of the three isomers in nitromethane was analysed by this method, with the following result:

	<i>ortho</i>	<i>meta</i>	<i>para</i>
Known composition (%)	43.0	10.8	46.2
Calc. from spectra	42.8	11.6	46.1

The isomeric composition of the mixture of chlorophenyl benzoates obtained in experiment (b) was: *ortho*, 35.7; *meta*, 12.9; *para*, 51.4%.

(ii) *Chlorodiphenyls.* The mixture of chlorodiphenyls which was obtained in experiment (h) was analysed according to the method used by Augood *et al.*¹⁴ The isomeric composition was found to be as follows: 2-, 59.6; 3-, 24.2; 4-, 16.2%.

(iii) *Chlorophenyl benzoates-phenyl benzoate-mixture.* Phenyl benzoate has a strong absorption peak at 13.28 μ , and this was found to be suitable for the analysis, despite its proximity to

¹⁴ Augood, Hey, and Williams, *J.*, 1953, 44.

the 13.18 μ peak for *p*-chlorophenyl benzoate. Analysis of prepared mixtures of known compositions showed that the method was accurate within $\pm 2\%$. Analysis of the mixture which was obtained in experiment (f) gave the following result: *o*-chlorophenyl benzoate, 24.0; *m*-, 7.2; *p*-, 32.5; phenyl benzoate, 36.3%. The isomer ratios for the esters were: *ortho*, 37.7; *meta*, 11.3; *para*, 51.0%. These are in good agreement with the ratios found for the product from the non-competitive experiment, *viz.*, *ortho*-, 35.7; *meta*, 12.9; *para*, 51.4%.

Reference compounds. Pure reference compounds for the above analyses were prepared as follows: chlorodiphenyls by the methods described by Augood *et al.*;¹⁴ chlorophenyl benzoates from the corresponding purified phenols by Schotten-Baumann reactions. M. p.s of solids and refractive indices of liquids agreed with recorded values.

Hydrolyses.—(a) *Silver iodide dibenzoate.* The complex was prepared from silver benzoate (10.35 g., 0.04517 mole) and iodine (5.732 g., 0.02259 mole) in nitrobenzene (150 ml.). Water (5 ml.) was added and the mixture was stirred at 20° for 1 hr., during which no gas was evolved. Filtration gave a solid which was treated with dilute ammonia solution, to give silver iodide (8.75 g., 0.3723 mole). Nitric acid (10N) was added to the ammoniacal filtrate until a precipitate began to be formed; sufficient ammonia was then added just to redissolve this. The addition of a slight excess of potassium iodide solution gave silver iodide (1.68 g., 0.00715 mole). 2-Ml. aliquot parts of the filtrate from this precipitation were acidified with sulphuric acid (2N) and treated with an excess of potassium iodide solution. The liberated iodine was estimated by titration with sodium thiosulphate solution. The whole solution was calculated to contain 0.00727 mole of iodate. No silver benzoate was detected. Extraction of the nitrobenzene solution with sodium hydrogen carbonate solution gave benzoic acid (5.5 g., 0.0444 mole).

(b) *Silver bromide dibenzoate.* The complex was prepared from silver benzoate (23.70 g., 0.1030 mole) and bromine (8.280 g., 0.0515 mole) in chlorobenzene (200 ml.). Hydrolysis with water (10 ml.) as above gave silver bromide (0.0955 mole), silver benzoate (0.0029 mole), silver bromate (0.00326 mole), and benzoic acid (0.077 mole). After removal of the nitrobenzene by fractional distillation under reduced pressure, a pitch-like solid remained, 1.0 g. of which distilled at 100–130°/1 mm. It was not further examined. Gas was evolved during the hydrolysis, and a further experiment showed that this was oxygen. The hydrolysis of 0.012 mole of silver bromide dibenzoate gave 45 ml. of oxygen (at N.T.P.). No perbenzoic acid was detected.

DISCUSSION

We preface this discussion by drawing attention to certain necessary assumptions. The solubilities of the silver halide dibenzoates in cold aromatic solvents are low (*e.g.*, silver bromide dibenzoate in chlorobenzene: 0.005 mole/l. at 20°), although they are sufficiently high in the hot solvents to permit recrystallisation.⁸ Since it would have been impracticable to work with volumes of aromatic solvents sufficient to effect complete dissolution of the reagents, it has been assumed that, under the heterogeneous conditions employed, the reactions occur very largely between molecules in solution, and that any reactions at the surface of undissolved reagent do not introduce additional discrimination between different aromatic molecules or between different positions in any one molecule.

Some of the present results are summarised in Tables 1 and 2. The aromatic substrates are arranged in downward order of increasing nucleophilic character.

From the following Tables, it may be seen that three different substitution reactions are

TABLE 1. *Yields (%) of products from the reactions between silver bromide dibenzoate and aromatic compounds, ArH.*

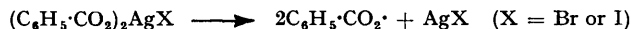
ArH	Temp.	PhAr	Ph·CO ₂ Ar	ArBr	Ph·CO ₂ H	Ph·CO ₂ Ag	AgBr	Ph·CO ₂ Ar/ ArBr	Recoveries (%)		
									Ph	Br	Ag
Ph·NO ₂ ...	45°	4	9	0.0	61.5	14.5	83.0	Very high	88.5	83.0	97.5
PhCl ...	20	0.0	25.0	0.0	32.0	17.0	80.0	Very high	74.0	80.0	97.0
PhH	20	0.0	25.0	2.0	31.0	23.5	74.5	12.5	79.5	76.5	98.0
PhBu ^t ...	20	0.0	6	3	43.5	29.5	69.0	2	78.5	72.0	98.5
PhOMe...	20	0.0	1	21.5	40.5	44.0	55.5	0.05	85.5	78.0	99.5

liable to occur, *viz.*, (a) phenylation, (b) benzoyloxylation, and (c) halogenation. Of these, (a) is considered to be a *homolytic* process which involves an initial thermal decomposition

TABLE 2. Yields (%) of products from the reactions between silver iodide dibenzoate and aromatic compounds, ArH.

ArH	Temp.	PhAr	Ph·CO ₂ Ar	ArI	Ph·CO ₂ H	Ph·CO ₂ Ag	AgI	Recoveries (%)		
								Ph	I	Ag
Ph·NO ₂ ...	130°	17.5	13.5	0.0	47.5	5.5	92.5	84.0	92.5	98.0
PhCl	132	21.0	8.0	0.0	38.5	9.0	89.0	76.5	89.0	98.0
PhH	80	25.0	1	0.5	40.5	2.5	94.5	69.0	95.0	97.0
PhOMe ...	100	0.0	1	37.5	47.0	42.0	56.0	90.0	93.5	98.0

of the reagent to give free benzoyloxy radicals: these, by decarboxylation, give phenyl radicals which then phenylate the aromatic solvent in the usual way.



Evidence for this mechanism is provided by the data in Table 3 where the ratios of isomers found in one of the present phenylation reactions are compared with those reported by Augood, Hey, and Williams for a typical homolytic phenylation.

TABLE 3. Phenylation of chlorobenzene. Isomer ratios (%).

Reagent	<i>ortho</i>	<i>meta</i>	<i>para</i>
Dibenzoyl peroxide (80°) ¹⁴	62.2	24.0	13.8
Silver iodide dibenzoate (132°)	60.0	24.0	16.0

These ratios agree within the limits of accuracy of the analytical method (estimated¹⁴ to be $\pm 3\%$), and we have no doubt that the active reagent is the same in each case. The temperature difference is probably unimportant, for, where comparison has been made, the orientation in homolytic phenylation appears not to be markedly temperature-dependent.¹⁵ It is to be noted that the evolution of significant quantities of carbon dioxide was observed in the present work only when the reaction led to phenylation of the solvent.

When phenyl radicals are produced in aromatic solvents by decarboxylation of benzoyloxy radicals, some slight benzoyloxylation always accompanies phenylation: in nitrobenzene,¹⁶ the ratio is *ca.* 1 : 6. In all the present cases, the proportion of benzoyloxylation has been too high to allow a derivation solely from attack by free benzoyloxy radicals. Indeed, in the benzoyloxylation of chlorobenzene by silver bromide dibenzoate, no phenylation whatever was detected (traces of chlorodiphenyls can be easily recognised by their persistent and characteristic odour); and we are satisfied that there was here no significant production of free phenyl radicals. Evidence relevant to the character of this benzoyloxylation is given in Table 4. Comparison is made with published data for nitration, the only example of electrophilic substitution in chlorobenzene for which suitable quantitative data are available.

From the results in Table 4, the partial rate factors for the benzoyloxylation of chlorobenzene are as follows: *ortho*, 0.36 ± 0.03 ; *meta*, 0.13 ± 0.01 ; *para*, 1.05 ± 0.11 . It may

TABLE 4. Isomer ratios (%) and total rate factors for the benzoyloxylation and nitration of chlorobenzene.

Reagent	<i>ortho</i>	<i>meta</i>	<i>para</i>	$F_{\text{C}_6\text{H}_4\text{Cl}}^{\text{C}_6\text{H}_5\text{CO}_2}$
Acetyl nitrate in acetic anhydride (25°) ¹⁷	31.0	—	69.0	0.0353
Acetyl nitrate in nitromethane (25°) ¹⁸	29.6	0.9	69.5	—
Silver bromide dibenzoate (20°)	35.5	12.9	51.4	0.34 ± 0.03

be seen that benzoyloxylation occurs mainly in the positions *ortho* and *para* to chlorine, and that the *ortho* and *meta* positions are deactivated. The net effect of the halogen on

¹⁵ Hey, Stirling, and Williams, *J.*, 1954, 2747.

¹⁶ Personal communication from Dr. G. H. Williams.

¹⁷ Bird and Ingold, *J.*, 1938, 918.

¹⁸ Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

benzoyloxylation at the *para*-position appears to be very small. Benzoyloxylation appears to resemble nitration in broad outline, although the former reaction is evidently less affected by the presence of the chlorine substituent. These results, coupled with the fact that only the *meta*-isomer could be isolated from the benzoyloxylation of nitrobenzene, lead us to classify benzoyloxylation as an *electrophilic* substitution reaction (with the complication mentioned above that in cases where the reagent also suffers thermal decomposition, some slight additional homolytic benzoyloxylation of unknown orientation is likely to occur). The unexpectedly high proportion of benzoyloxylation which was observed in the reaction between silver iodide dibenzoate and nitrobenzene is inconsistent with a homolytic mechanism. It may plausibly be attributed to the high dielectric constant of this solvent (36) in comparison with that of chlorobenzene (5.6) and benzene (2.3). This factor should favour the heterolytic benzoyloxylation at the expense of homolytic reactions, thereby compensating for the low nucleophilic reactivity of nitrobenzene.

The halogenation reaction (c) predominates in anisole, but has also been detected in benzene and *tert.*-butylbenzene. It has the character of an *electrophilic* substitution. Thus, silver bromide dibenzoate reacted with anisole to give *p*-bromoanisole which was virtually free from the *ortho*- and the *meta*-isomer, and the iodoanisole obtained with the use of silver iodide dibenzoate contained not less than 94% of the *para*-isomer. Slight benzoyloxylation of anisole was also detected—insufficient to permit measurement of the isomer ratios.

From the foregoing considerations, we conclude that there is a balance between the tendency for the silver halide dibenzoates to decompose thermally, giving free radicals, and their ability to undergo electrophilic substitution reactions with the aromatic solvent. With silver iodide dibenzoate, the balance seems to favour thermal decomposition, and it was only in anisole, the most nucleophilic solvent of those examined, that this reagent failed to give phenylation products.

With increasing nucleophilic character of the aromatic substrate (Table 1), the ratio of bromination to benzoyloxylation increases in a way which appears to require a purely chemical explanation and seems relevant to the general question of the relative reactivities of electrophilic reagents in aromatic substitutions. The silver halide dibenzoates may be regarded as reagents having two electrophilic functions which can compete for an excess of an aromatic substrate. Hence it has been possible to compare the relative velocities of two electrophilic substitutions under identical conditions.

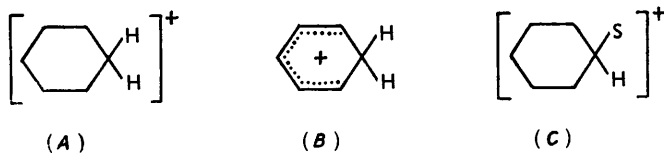
The problem of differing "activities" of various electrophilic reagents in aromatic substitutions has been considered by Brown and Nelson¹⁹ (cf. de la Mare²⁰). Brown and Nelson suggest that the least "active" electrophilic reagents are those in which the attacking cation is of low energy or is not well developed, and that such reagents require the greatest contribution from the nuclear electrons to the partly formed bond in the transition state. Reagents of lowest "activity" should take the greatest advantage from the electromeric effects of suitable substituents in the aromatic ring. This conception of "activity" seems inadequate to explain some of the present results. Thus, if benzoyloxylation of chlorobenzene is faster than bromination for the main reason that it is the better able to take advantage of electromeric release from chlorine, we should expect it to have a similar advantage in anisole. The observed reversal of the relative rates seems to imply the operation of some effect which, in passing from chlorobenzene to anisole, bears disproportionately on the energies of the transition states of benzoyloxylation and bromination. Suggestions regarding the nature of this effect must necessarily be rather speculative at the present stage; but the results suggest to us that transition-state conjugation involving the *entering* substituent may be an important factor. Muller, Pickett, and Mulliken²¹ have recently calculated by a molecular-orbital method that the hyperconjugation energy of the ion (*A*) makes a considerable contribution to its total resonance energy. The classical structure (*B*) appears to be an inexact representation, and the ring must be credited with partial aromatic character. The above workers pointed out the

¹⁹ Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

²⁰ de la Mare, *J.*, 1949, 2871.

²¹ Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4770.

relevance of their calculations to the general case of the ions (C), which are believed to exist as intermediates in electrophilic substitutions ($S = \text{NO}_2, \text{Br}, \text{etc.}$). If these ions also have some (probably less) aromatic character, overlap between the π -electrons of the ring and any p -electrons on S would be a stabilising factor. Since the structures of these



ions are probably close to those of the transition states for their formation, such overlap would act to reduce the activation energy for an electrophilic substitution. It should increase in importance as the hybridisation of the C atom at the point of substitution approaches sp^2 , *i.e.*, as the recession of H^+ enables the C-S bond to shorten and to approach the plane of the ring. It follows that any stretching of the aromatic C-H bond in the transition state should have the greatest kinetic effect in cases where the entering substituent has the greatest conjugative ability. The fact that energy considerations favour a degree of proton loss in such cases does not of course prove that this occurs in practice; but if it does occur, the entry of highly conjugating substituents should be governed, not only by the availability of electrons at the site of substitution, but also to some extent by the ease of proton loss. The requirements for these are opposed. Where both are important, the activating or deactivating effects of existing substituents should tend to be less.

For the reasons outlined by Ingold,²² it seems probable that an oxygen-containing group such as benzyloxy is much better able to conjugate with an aromatic system than is bromine. Therefore, loss of the aromatic proton should have potentially the greater kinetic significance in benzyloxylation,* and the velocity of this reaction should be less affected by existing substituents. The results accord with this. Benzyloxylation is the faster reaction in chlorobenzene, which is deactivated, whereas bromination is the faster in anisole, which is activated. In benzene, benzyloxylation is faster than bromination, and the point at which both reactions become equally fast is evidently a degree of nucleophilic reactivity of the solvent close to that of *tert.*-butylbenzene. Benzyloxylation is less selective than nitration, and shows a higher total rate factor (Table 4). Since it has been shown that the loss of the aromatic proton is kinetically insignificant in nitration²³ and in bromination (under conditions different from ours),²⁴ the difference in selectivity accords with the present suggestions and with those made by Brown and Nelson.¹⁹ However, where differences in reactivity are mainly due to differences in transition-state conjugation, rather than to differences between the (Lewis) acidities of the attacking reagents, we should not expect the intrinsically slowest reactions to be necessarily the most discriminating between different nuclear positions. We do not suggest that this conjugation is the only, or generally even the main, factor which determines the "activities" of different attacking reagents. Brown and Nelson's suggestions¹⁹ seem to provide a satisfactory explanation when proton loss is kinetically unimportant. Transition-state conjugation may perhaps be more generally important in homolytic substitution, where polar influences are less significant.

Hydrolysis of the Complexes.—This was examined in order to ascertain whether silver benzoate is a true product of the reactions with aromatic compounds (Tables 1 and 2). Since little or no silver benzoate was found after hydrolysis, it could not have been present before the reactions with aromatic compounds. Wieland and Fischer⁶ reported that silver iodide dibenzoate is hydrolysed according to the equation: $3(\text{Ph}\cdot\text{CO}_2)_2\text{AgI} + 3\text{H}_2\text{O} \longrightarrow 6\text{Ph}\cdot\text{CO}_2\text{H} + 2\text{AgI} + \text{AgIO}_3$. We obtained the following

* A hydrogen-isotope effect is to be expected if our suggestions are correct.

²² Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 73 *et seq.*

²³ Melander, *Nature*, 1949, **163**, 599.

²⁴ *Idem*, *Arkiv Kemi*, 1950, **2**, 211.

yields, which are in good agreement with this equation (calculated figures in parentheses) : benzoic acid, 98.2 (100); silver iodide, 82.4 (83.3); silver iodate, 16.1 (16.7) mol. %. The hydrolysis of silver bromide dibenzoate does not proceed in an exactly analogous manner. The yields in this case were : benzoic acid, 78.0; silver bromide, 92.8; silver bromate, 3.2; silver benzoate, 2.8 mol. %; unidentified neutral products were formed, and oxygen was evolved in 35% of the amount to be expected if silver hypobromite had been initially formed and had then reacted thus, $2\text{AgOBr} \longrightarrow 2\text{AgBr} + \text{O}_2$, in preference to $3\text{AgOBr} \longrightarrow 2\text{AgBr} + \text{AgBrO}_3$.

Structure of the Complexes.—It seems to be generally agreed, following Simonini,⁵ that the reagents have the formula $(\text{Ph}\cdot\text{CO}_2)_2\text{AgBr}$. The hydrolysis results support this formula for the iodide, although they are inconclusive in the case of the bromide. Crawford and Simonds⁷ have recently confirmed an analogous formula for the similar complexes formed from silver fluorocarbon-carboxylates and iodine. The stability and absence of colour rule out any structure containing Ag^{2+} or Ag^{3+} . Prévost²⁵ suggested an ion-pair structure $\text{I}^+[\text{Ag}(\text{R}\cdot\text{CO}_2)_2]^-$ which resembles that usually written for such double salts as, e.g., $\text{K}^+[\text{Ag}(\text{CN})_2]^-$. Prévost's structure can explain the electrophilic halogenations but cannot account for the electrophilic benzoyloxylation. The latter can be understood if the complexes are in fact able to react in the alternative form, e.g., $\text{Ph}\cdot\text{CO}_2^+[\text{Ag}(\text{O}_2\text{C}\cdot\text{Ph})\text{I}]^-$ at the demand of a suitable reagent. However, it is also possible to draw feasible structures in which the silver forms part of a complex cation, and which conform equally well with the known chemical reactions and physical properties. We reserve further discussion of this point.

The authors thank Professor D. H. Hey, F.R.S., for his helpful interest. One of them (P. C.) thanks the Ministry of Education for a grant.

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[Received, February 7th, 1956.]

²⁵ Prévost, *Compt. rend.*, 1935, **200**, 942.