

645. *Homolytic Aromatic Substitution. Part XXX.* The Phenylation of Methyl Benzoate. The Use of Methyl Benzoate in Competitive Reactions.*

By D. H. HEY, F. C. SAUNDERS, and GARETH H. WILLIAMS.

Measurements are reported of the ratios of isomers formed in the phenylation of methyl benzoate, both alone and in admixture with nitrobenzene, and of nitrobenzene in admixture with methyl benzoate. Partial rate factors for the phenylation of methyl benzoate are also obtained from the results of these experiments. The results confirm the previous conclusion that isomer ratios are unaffected by the presence of other aromatic solvents.

PREVIOUS work on the phenylation of benzotrichloride¹ showed that the resulting mixture of isomeric trichloromethylbiphenyls could be analysed by quantitative hydrolysis and methylation to give the corresponding methyl biphenylcarboxylates. The same method has now been applied to the phenylation of methyl benzoate. The presence of the hydrolysable ester group in the phenylated product facilitates the removal and isolation of biaryls containing this group from a mixture of substituted biaryls, and an investigation was therefore carried out into the possible use of methyl benzoate as a sub-standard in competitive reactions. With methyl benzoate as a sub-standard, it should also be possible to measure the rate ratio and the isomer ratio directly in a single competitive reaction, and in this way the possible existence of solvent interaction in competitive reactions might be brought to light. The present Paper records the results obtained in the phenylation of methyl benzoate with benzoyl peroxide, and in competitive reactions with methyl benzoate–nitrobenzene mixtures with benzoyl peroxide.

EXPERIMENTAL

Benzoyl peroxide and nitrobenzene were purified as described in Part II.² Methyl benzoate was shaken with saturated aqueous sodium hydrogen carbonate and then with water. It was dried (K_2CO_3), filtered, and collected at 79–80°/10–12 mm.

The infrared spectrographic measurements were carried out on a Grubb-Parsons double-beam instrument.

The Decomposition of Benzoyl Peroxide in Methyl Benzoate.—Benzoyl peroxide (6 g.) in methyl benzoate (200 g.) was maintained at 80° for 72 hr., after which the mixture was extracted in the cold with saturated aqueous sodium hydrogen carbonate (5 × 50 ml.). The organic layer was washed with water and dried ($CaCl_2$), and the aqueous alkaline extract was acidified to give benzoic acid. Excess of methyl benzoate was removed by distillation, and the residue was twice boiled under reflux for 14 hr. with 10% aqueous sodium hydroxide. The mixture was extracted with benzene, and the combined alkaline solutions were filtered and acidified. The liberated acids were extracted with ether, esterified with diazomethane, and distilled, as described in Part XXI.¹ This reaction was carried out in duplicate and the results are reported in Table 1.

The biaryl fraction, which on the basis of earlier work¹ can contain only methyl biphenylcarboxylates, was analysed by the infrared spectroscopic method. As a result of the higher proportion of methyl biphenyl-2-carboxylate compared with that found in the mixtures from the phenylation of benzotrichloride,¹ the analytical procedure described by Augood, Hey, and Williams³ was found to be suitable in this instance. Measurements of optical density were made at 794.9 and 863.6 cm^{-1} , which are absorption maxima for the *ortho*- and *para*-isomers, respectively. The proportion of the *meta*-isomer was obtained by difference. Nitromethane was used as solvent. The results are in Table 2, which also includes the figures obtained with a synthetic mixture of known composition.

Competitive Experiments with Nitrobenzene–Methyl Benzoate Mixture.—Benzoyl peroxide

* Part XXIX, *J.*, 1963, 5612.

¹ Hey, Saunders, and Williams, *J.*, 1961, 554.

² Augood, Hey, and Williams, *J.*, 1952, 2094.

³ Augood, Hey, and Williams, *J.*, 1953, 44.

(6 g.) in an equimolar mixture of nitrobenzene (81.2 ml.) and methyl benzoate (98.8 ml.) was maintained at 80° for 72 hrs. The free benzoic acid was extracted with aqueous sodium hydrogen carbonate. The organic solution was dried (Na₂SO₄), and excess of the solvents was removed under reduced pressure. The residue was boiled under reflux for 14 hr. with 10%

TABLE 1.
Decomposition of benzoyl peroxide in methyl benzoate.

Experiment	1	2
Free benzoic acid (g.)	0.58	0.59
Methyl biphenylcarboxylates (g.)	2.681	2.438
Residue (g.)	1.505	1.317

TABLE 2.
Isomer ratios of methyl biphenylcarboxylates.

	<i>ortho</i>	<i>meta</i>	<i>para</i>
Experiment { 1	56	19	25
Experiment { 2	58	16	26
Mean	57	17.5	25.5
Synthetic mixture { Found	52	18	30
Synthetic mixture { Calc.	48	23	29

TABLE 3.

Products from phenylation of nitrobenzene-methyl benzoate mixture.

Experiment	3	4
Free benzoic acid (g.)	2.57	2.67
Methyl biphenylcarboxylates (g.)	1.519	1.506
Residue (g.)	0.247	0.261
Nitrobiphenyls (g.)	2.340	2.363
Residue (g.)	0.383	0.346

aqueous sodium hydroxide (100 ml.). The alkaline layer was separated and acidified with hydrochloric acid. The precipitated acids were extracted with ether and esterified with ethereal diazomethane, as previously described. The mixture of esters was distilled, to give methyl benzoate (b. p. 70–80°/10–12 mm.) and the methyl biphenylcarboxylates (b. p. 75–85°/0.05 mm.). The organic layer was dried (Na₂SO₄), and distillation gave two fractions: (a) b. p. 80–85°/10–12 mm.; (b) b. p. 95–105°/0.05 mm. The former consisted of nitrobenzene (Found: N, 11.8. Calc. for C₆H₅NO₂: N, 11.4%) and the latter of a mixture of nitrobiphenyls (Found: N, 6.85. Calc. for C₁₂H₉NO₂: N, 7.0%). The reaction was carried out in

TABLE 4.
Isomer ratios of methyl biphenylcarboxylates from competitive experiment.

	<i>ortho</i>	<i>meta</i>	<i>para</i>
Experiment { 3	58	16	26
Experiment { 4	60	16	24
Mean	59	16	25

TABLE 5.
Isomer ratios of nitrobiphenyls from competitive experiment.

	<i>ortho</i>	<i>meta</i>	<i>para</i>
Experiment { 3	60	9.8	30.2
Experiment { 4	61	10.8	28.2
Mean	60.5	10.3	29.2
Synthetic mixture { Found	60	12.5	27.2
Synthetic mixture { Calc.	61.6	11.4	27.0

TABLE 6.

Experiment	$K_{\text{PhCO}_2\text{Me}}^{\text{PhNO}_2}$	$K_{\text{PhNO}_2}^{\text{PhCO}_2\text{Me}}$	$K_{\text{PhH}}^{\text{PhCO}_2\text{Me}}$
3	1.64	0.61	1.79
4	1.67	0.60	1.76
Mean	1.65(5)	0.60(5)	1.77(5)

duplicate and the results are in Table 3. No evidence was obtained of the existence of products derived from benzoyloxylation (*i.e.*, hydroxybenzenecarboxylic acids and nitrophenols).

Determination of Isomer Ratios.—The composition of the mixture of methyl biphenylcarboxylates was determined by means of infrared spectroscopy, as described above for the products of the phenylation of methyl benzoate. The results are in Table 4.

The composition of the mixture of nitrobiphenyls was also determined by infrared spectroscopy using the band at 789.3 cm⁻¹ for the *ortho*-isomer and that at 738.0 cm⁻¹ for the *meta*-isomer. Nitromethane was used as solvent. The method was tested with a synthetic mixture of known composition. The results are in Table 5.

The rate ratio for the phenylation of methyl benzoate can be calculated from the weights of nitrobiphenyls and methyl biphenylcarboxylates obtained in the competitive experiments together with the known rate ratio $K_{\text{PhH}}^{\text{PhNO}_2} = 2.94$ (ref. 4) and are shown in Table 6.

⁴ Hey, Orman, and Williams, *J.*, 1961, 565.

Using the isomer ratios $o:m:p = 57:17.5:25.5$ for the phenylation of methyl benzoate the following partial rate factors can be calculated for this reaction: $F_o = 3.04$; $F_m = 0.93$; $F_p = 2.72$.

DISCUSSION

No direct determination of the ratio of isomers formed in the phenylation of methyl or ethyl benzoate has been previously reported, but Dannley and his co-workers,^{5,6} measured the ratio of isomers formed in competitive experiments involving the use of benzoyl peroxide in relatively high concentration, under which conditions some of the free benzoic acid, formed in the decomposition of the peroxide, is phenylated. The resulting acids were esterified and their concentrations determined. With pyridine (which gives rise to salt formation) as one of the competing solvents, the proportions of isomers formed were *ortho* 49%; *meta* 20%; *para* 31%. With non-basic competing solvents the figures were: *ortho* 59%; *meta* 15%; *para* 26%. In the present work, a much more dilute solution of benzoyl peroxide in methyl benzoate was used in order to ensure as far as possible that all of the methyl biphenylcarboxylates arise from direct phenylation of methyl benzoate. The proportions of the isomeric methyl biphenylcarboxylates formed in this way were: *ortho* 58%; *meta* 17%; *para* 25%, which are close to the earlier values reported above

TABLE 7.
Isomer ratios for homolytic phenylation.

Substrate	Solvent system	Temp.	Isomer (%)			Reference
			2-	3-	4-	
PhNO ₂	PhNO ₂	80°	62	10	28	*
PhNO ₂	PhNO ₂ -C ₅ H ₅ N	105	63	11	26	†
PhCl	PhCl	80	50	32	18	‡
PhCl	PhCl-C ₅ H ₅ N	70	54	31	15	§
PhBr	PhBr	80	49	33	18	§
PhBr	PhBr-C ₅ H ₅ N	70	48.5	33	18.5	§
PhI	PhI	80	52	31	17	§
PhI	PhI-C ₅ H ₅ N	70	55	28	16.5	§
C ₅ H ₅ N	C ₅ H ₅ N	105	54	32	14	**
C ₅ H ₅ N	PhCl-C ₅ H ₅ N	70	58	28	14	§
C ₅ H ₅ N	PhBr-C ₅ H ₅ N	70	58	28	14	§
C ₅ H ₅ N	PhI-C ₅ H ₅ N	70	58	28	14	§

* Chang Shih, Hey, and Williams, *J.*, 1958, 1885. † Cadogan, personal communication.
‡ Chang Shih, Hey, and Williams, *J.*, 1958, 2600. § Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412. ** Hey, Stirling, and Williams, *J.*, 1955, 3963.

for the phenylation of free benzoic acid. The competitive experiment carried out on the phenylation of a mixture of methyl benzoate and nitrobenzene gave a figure of $K_{\text{PhNO}_2}^{\text{PhCO}_2\text{Me}} = 0.60(5)$, which in combination with $K_{\text{PhH}}^{\text{PhNO}_2} = 2.94$ gives $K_{\text{PhH}}^{\text{PhCO}_2\text{Me}} = 1.77(5)$. The partial rate factors for the phenylation of methyl benzoate are thus found to be: $F_o = 3 \times 1.77(5) \times 0.057 = 3.04$; $F_m = 3 \times 1.77(5) \times 0.175 = 0.93$; $F_p = 6 \times 1.77(5) \times 0.255 = 2.72$. These values indicate an activation of the *ortho*- and *para*-sites towards phenylation, as would be expected with a directing group which is conjugated with the nucleus.⁷

In the determination of partial rate factors for homolytic aromatic substitution, it has been customary in the past to determine the rate in a competitive experiment, usually with nitrobenzene as a sub-standard, and, because of the difficulty of separating the mixture of six biphenyl derivatives, to measure isomer ratios in reactions involving a single solvent. It is, of course, possible that the ratio of isomers is different in a mixed solvent as a result of interaction of the two solvents. If, however, one of the competing solvents contains a reactive centre which facilitates separation of the biaryl fraction, it should be possible to determine the relative rate and the isomer ratio in one and the same experiment. A comparison of such results with those obtained by the previous method should bring to light

⁵ Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445.

⁶ Dannley and Gregg, *J. Amer. Chem. Soc.*, 1954, **76**, 2997.

⁷ Williams, *Chem. and Ind.*, 1961, 1286.

any discrepancies which could be attributed to solvent interaction. Dannley *et al.*^{5,6} have already used this principle with the aid of pyridine as one of the solvents, and their results agree, within experimental error, with those reported earlier from our laboratories from reactions with single solvents as shown in Table 7. These results seem to indicate the absence of any significant solvent interaction.

When methyl benzoate is used as one of the competing solvents the mixture of six biaryls can be separated by hydrolysis into two mixtures each of three components. The

TABLE 8.
Isomer ratios for homolytic phenylation of methyl benzoate and nitrobenzene (80°).

Substrate	Solvent system	Isomer (%)			Reference
		2-	3-	4-	
PhCO ₂ Me	PhCO ₂ Me	57	17.5	25.5	This work
PhCO ₂ Me	PhCO ₂ Me-PhNO ₂	59	16	25	This work
PhNO ₂	PhNO ₂	62	10	28	*
PhNO ₂	PhCO ₂ Me-PhNO ₂	60.5	10.3	29.2	This work

* Chang Shih, Hey, and Williams, *J.*, 1958, 1885.

resulting biphenylcarboxylic acids can be quantitatively esterified and the mixture of esters analysed by infrared spectrophotometry or gas chromatography. The results obtained from the phenylation of nitrobenzene-methyl benzoate mixtures, and those for measurements made on single solvents, are shown in Table 8. These results again indicate the absence of any significant solvent interaction, and also lend support to the previous conclusion^{8,9} that isomer ratios measured in experiments with single solvents are unaffected by the formation of substantial amounts of high-boiling residues in these experiments.

Thanks are accorded to the Swansea Education Committee and the D.S.I.R. for maintenance grants to F. C. S.

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

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
MALET STREET, LONDON W.C.1.

[Received, November 7th, 1963.]

⁸ Morrison, Cazes, Samkoff, and Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.

⁹ Hey, Perkins, and Williams, *Chem. and Ind.*, 1963, 83.