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The Synthesis of Phenyl Carboxylates from *p*-Bromophenol and Carboxylic Acids

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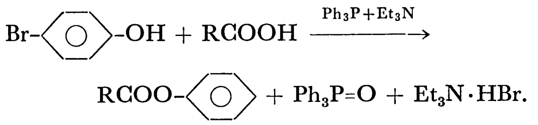
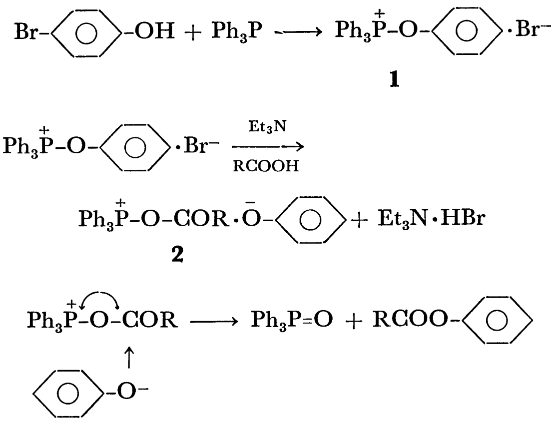
Synopsis. The reaction of *p*-bromophenol with carboxylic acids in the presence of triphenylphosphine and triethylamine proceeded at a high temperature, with the elimination of hydrogen bromide, to give phenyl carboxylates and small amounts of *p*-bromophenyl carboxylates.

We have recently reported that the direct esterification of phenols (ArOH) with carboxylic acids proceeds easily at room temperature by the use of both triphenylphosphine and carbon tetrachloride as dehydrating agents in the presence of triethylamine, giving only the corresponding aryl carboxylates (RCOOAr) such as *p*-bromophenyl benzoate from *p*-bromophenol and benzoic acid in a high yield.1) From our further investigation into the esterification of *p*-bromophenol, we have found that the esterification in the presence of triphenylphosphine and triethylamine gives phenyl carboxylates, with the elimination of hydrogen bromide:



The results are shown in Table 1. The reaction proceeds at a high temperature to give, simultaneously, phenyl carboxylate and small amounts of *p*-bromophenyl carboxylates. The yield of the phenyl carboxylates increased with an increase in the reaction temperature, but the yield of *p*-bromophenyl carboxylates decreased conversely. A black-colored, tarry product was produced in the absence of triethylamine, and the use of pyridine instead of triethylamine gave phenyl carboxylate in a poor yield. Also, the esterification with carboxylic acid having a nitro group resulted in the formation of a tarry product in contrast to the expected ester.

It is concluded that the esterification of *p*-bromophenol with carboxylic acids in the presence of triphenylphosphine and triethylamine proceeds through the process shown in the following scheme:



It has been reported by Hoffmann that the phosphonium salt (**1**) assumed as an intermediate is formed by the elimination of bromine from *p*-bromophenol with triphenylphosphine at a high temperature.2) The resulting salt **1** is converted to acyloxytriphenyl-

Table 1. Phenyl and *p*-bromophenyl carboxylates a)

RCOOH	Reaction temp	Phenyl esters					*p*-Bromophenyl esters				
		Yield	Mp	IR(ν/cm⁻¹)		MS(*m/e*)	Yield	Mp	IR(ν/cm⁻¹)		MS(*m/e*)
R	°C	%	°C	C=O	C-O	M+	%	°C	C=O	C-O	M+
CH_3	200	50	82—83/10b)	1770	1230	136	0				
CH_3	170	46	84—86/12b)	1770	1230	136	13	122—124/11b)	1770	1230	214
CH_3 c)	200			Tarry product was formed							
$CH_3CH_2CH_2$	200	62	106—108/8b)	1770	1205	164	4	—	1770	1205	242
C_6H_5	200	84	70—72	1725	1265	198	0				
C_6H_5	170	62	71—72	1725	1265	198	12	104—106	1740	1260	276
C_6H_5 d)	170	9	70—73	1725	1265	198	21	105—106	1740	1260	276
p-ClC_6H_4	200	64	100—102	1735	1280	232	0				
p-ClC_6H_4	170	54	101—103	1735	1280	232	4	100—104	1750	1270	310
o-ClC_6H_4	200	40	37—38	1735	1280	232	0				
p-$CH_3C_6H_4$	200	75	71—73	1735	1275	212	14	95—97	1740	1270	290
p-$CH_3OC_6H_4$	200	62	67—69	1730	1275	228	5	103—105	1730	1270	306
p-$NO_2C_6H_4$	200			Tarry product was formed							
C_6H_5CH=CH	200	58	74—76	1730	1205	224	5	111—114	1750	1215	302

a) Reaction time: 4 h. b) Bp: °C/Torr (1 Torr = 133.322 Pa). c) In the absence of triethylamine. d) Pyridine was used instead of triethylamine.

phosphonium phenoxide (**2**) by the nucleophilic attack of the acyloxy anion onto the phosphorus atom of **1**, followed by the attack of the phenoxy anion onto the carbonyl carbon of **2**, giving phenyl carboxylate with the elimination of triphenylphosphine oxide. Otherwise, it is considered that the formation of *p*-bromophenyl carboxylate is by the attack of *p*-bromophenol on **2**.

Experimental

All the melting and boiling points are uncorrected. All the chemicals used were of an analytical reagent-grade. The thin-layer chromotography (TLC) was performed on Merck's silica gel 60 (70—230 mesh). The IR spectra were recorded in KBr on a Shimadzu IR-27C spectrometer, and the MS, on a Hitachi RM-50GC spectrometer with 60 eV.

General Procedure. A mixture of triphenylphosphine (5.5 mmol), triethylamine (5.5 mmol), carboxylic acid (5.5 mmol), and *p*-bromophenol (5.0 mmol) was heated at 200 °C for 4 h in the absence of a solvent. After hexane has been poured into the resulting mixture, the insoluble triphenylphosphine oxide and triethylamine hydrobromide were filtered off. The filtrate was washed with an aqueous sodium hydroxide solution, dried over anhydrous sodium sulfate, and concentrated, thus giving an ester. The pure ester was obtained by recrystallization from hexane or methanol, or by chromatography on silica gel, and was determined by infrared and mass-spectral analysis.

References

1) S. Hashimoto and I. Furukawa, *Bull. Chem. Soc. Jpn.*, **54**, 2227 (1981).

2) H. Hoffmann, L. Horner, H. G. Wippel, and D. Michael, *Chem. Ber.*, **95**, 523 (1962).