

## A Novel Synthesis of Phenyl Carboxylates

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(Received December 12, 1980)

**Synopsis.** The direct synthesis of phenyl carboxylates from phenols and carboxylic acids is reported. The reactions proceeded easily when triphenylphosphine and carbon tetrachloride were used as dehydrating agents in the presence of a tertiary amine at room temperature, thus giving esters in high yields.

It has been known that the direct synthesis of phenyl carboxylates from carboxylic acids and phenols usually fails in the presence of common mineral acids. Therefore, the reaction has been carried out by using a special catalyst such as polyphosphoric acid,<sup>1)</sup> a combination of boric acid and sulfuric acid,<sup>2)</sup> and polymer-protected aluminium chloride<sup>3)</sup> under heating. However, these methods can not be applied to the esters, which are unstable to heat and acid.

We have now investigated the direct acylation of phenols with acids under mild conditions, and have found that the reaction proceeds easily to form phenyl carboxylates when a combination of triphenylphosphine and carbon tetrachloride is used as the dehydrating agent in the presence of triethylamine. The results are shown in Table 1.

Although the reaction proceeded easily at room temperature to give esters in high yields, phenol and acid having a nitro group afforded the esters in a poorer yield because of the simultaneous formation of a colored matter from the phosphine and nitro

compound.

Ester formation by the use of triphenylphosphine and carbon tetrachloride was investigated by Appel<sup>4)</sup> for the esterification of an alcohol with a carboxylic acid. In this case, a high yield is obtained only when alcohol is added as the last component after reacting phosphine, carboxylic acid, and carbon tetrachloride in the presence of tertiary amine, when the alcohol and acid are added simultaneously into a mixture of phosphine, carbon tetrachloride and tertiary amine, the yield of the ester decreases because of the simultaneous formation of both alkyl halide and ester. On the other hand, the acylations of phenols with carboxylic acids in our work gave only esters in high yields, even when all reactants were reacted simultaneously. This difference may be attributed to the fact that phenol attacks selectively only the carbonyl carbon in the acyloxyphosphonium salt [II] assumed as an intermediate, while alcohol attacks both the phosphorus and the carbonyl carbon.<sup>4)</sup>

From these results, we concluded that the esterification of phenols with carboxylic acids in the presence of a tertiary amine, when triphenylphosphine and carbon tetrachloride are used as dehydrating agents, proceeds through the process shown in the following scheme:

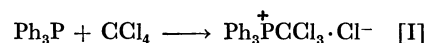
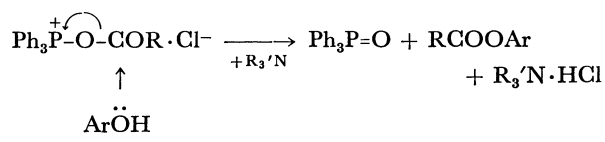
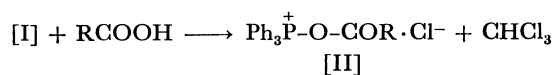


TABLE 1. PHENYL CARBOXYLATES

RCOOC <sub>6</sub> H <sub>4</sub> X		Yield %	Mp/°C (Torr)	Analysis		
R:	X:			IR		MS( <i>m/e</i> ) M <sup>+</sup>
				$\bar{\nu}(\text{C}=\text{O})$ cm <sup>-1</sup>	$\bar{\nu}(\text{C}-\text{O})$ cm <sup>-1</sup>	
CH <sub>3</sub>	H	97	82—83 (10)	1770	1230	136
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	H	90	107 (8)	1770	1205	164
C <sub>6</sub> H <sub>5</sub>	H	91	70—71	1725	1265	198
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	85	100.5—101.5	1735	1280	232
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	92	70.5—72.5	1735	1275	212
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	H	87	67.5—69	1730	1275	228
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	34	107.5—111	1755	1280	243
C <sub>6</sub> H <sub>5</sub> CH=CH	H	86	74—75.5	1730	1205	224
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Cl	89	84—86	1745	1285	232
C <sub>6</sub> H <sub>5</sub>	<i>m</i> -Cl	92	69.5—70.5	1740	1260	232
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Br	72	104—106	1740	1260	276
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub>	78	70—71	1725	1275	212
C <sub>6</sub> H <sub>5</sub>	<i>m</i> -CH <sub>3</sub>	89	51.5—53.5	1740	1270	212
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> O	85	84—86	1735	1275	228
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -NO <sub>2</sub>	13	140—142	1750	1230	243
CH <sub>3</sub>	<i>p</i> -Br	87	122—125 (11)	1770	1230	214
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	<i>p</i> -Br	66	144—149 (11)	1770	1205	242
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -Br	70	100—104	1750	1270	310
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -Br	85	72—75.5	1760	1245	310
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>p</i> -Br	81	94—98	1740	1270	290
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -Br	62	103—104.5	1730	1270	306
C <sub>6</sub> H <sub>5</sub> CH=CH	<i>p</i> -Br	79	113—115	1750	1215	302



### Experimental

All the melting and boiling points are uncorrected. All the chemicals used were of an analytical reagent grade. Thin-layer chromatography (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.

*Procedure.* A mixture of benzoic acid (24 mmol), phenol (20 mmol), carbon tetrachloride (24 mmol), triethylamine (24 mmol), and triphenylphosphine (24 mmol) in 30 ml of acetonitrile was stirred at room temperature for 4 h.

After the acetonitrile has been evaporated, hexane was added to the residue. The hexane solution was filtered off to remove the triphenylphosphine oxide and triethylamine hydrochloride precipitated, washed with an aqueous sodium hydroxide solution, and dried over anhydrous sodium sulfate, and then the hexane was removed. Subsequent distillation or recrystallization of the residual solid gave 3.6 g of phenyl benzoate (91% yield) as white crystals: mp 70–71 °C. A similar procedure has been applied successfully to a variety of substituted phenols, aliphatic, and aromatic carboxylic acids. The resulting products were identified by means of infrared and mass spectral analysis.

### References

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