The Preparation of Aryl Imidates and Diaroylamides by Phase-Transfer Catalysis

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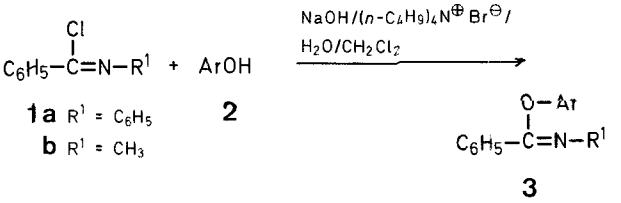
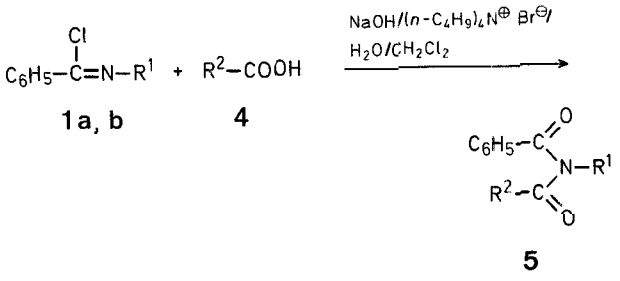
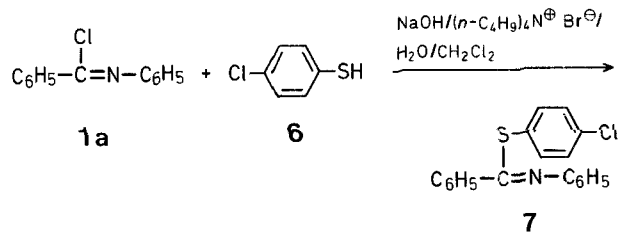
Phase-transfer catalysis has aroused considerable interest as a synthetic tool in recent years[1,2]. In this communication we report the application of the technique to the preparation of aryl imidates **3** by the reaction of sodium phenoxides with imidoyl chlorides **1**, and to the preparation of diaroyl amides **5** by the reaction of the sodium salt of carboxylic acids **4** with imidoyl chlorides **1**. In both cases tetrabutylammonium bromide was used as the phase transfer catalyst. Recently, the preparation of imidoyl cyanides was reported[3] and this paper extends the use of imidoyl chlorides as synthetic intermediates under phase-transfer conditions. Imidoyl isothiocyanates can also be prepared by the methods described here.







Aryl imidates have been prepared previously by treating the phenol with sodium ethoxide in absolute ethanol and then adding the imidoyl chloride in ether[4]. The method reported here is more convenient, and eliminates the formation of the alkoxyimidate as a competing product.

Mumm[5,6] was the first to prepare diaroylamides by treating an imidoyl chloride with the salt of a carboxylic acid. However he gave few practical details, and as shown here, this preparation is ideally suited to the phase-transfer technique. In this reaction, the initially formed *O*-acylisoimide undergoes a rapid thermally induced rearrangement[6] to the *N*-acyl compound, through a [1,3] acyl migration. Another recent method[7] involves the formation of the *N*-lithioamide by reaction of the amide with butyllithium, followed by reaction with the acid chloride. The method reported here is obviously much more convenient and led to better yields of products.

N-Phenylbenzamide and *N*-methylbenzamide were converted to the corresponding imidoyl chlorides by reaction with a slight excess of thionyl chloride.

2-Naphthyl *N*-Methylbenzimidate; Typical Procedure:
N-Methylbenzimidoyl chloride (**1b**; 0.25 g, 1.6 mmol) in dichloromethane (10 ml) is added to a rapidly stirred solution of 2-naphthol (**2**; 0.30 g, 2.1 mmol), sodium hydroxide (0.082 g, 2.1 mmol), and tetrabutylammonium bromide (0.020 g, 0.06 mmol) in water (6 ml) and the mixture stirred at room temperature for 1 h. The mixture is diluted with chloroform (20 ml), the organic layer separated, and washed successively with 5% sodium hydroxide and water, dried with anhydrous sodium sulphate, and evaporated to give the crude product which is recrystallized from ethanol; yield: 0.34 g (80%); m.p. 62–63 °C.

$C_{18}H_{15}NO$	calc.	C 82.73	H 5.79	N 5.36
(261.3)	found	82.49	5.86	5.54

Preparation of *N*-(3-Nitrobenzoyl)-*N*-phenylbenzamide; General Procedure:
N-Phenylbenzimidoyl chloride (**1a**; 0.28 g, 1.3 mmol) in dichloromethane (10 ml) is added to a rapidly stirred solution of 3-nitrobenzoic acid (0.24 g, 1.4 mmol), sodium hydroxide (0.055 g, 1.4 mmol), and tetrabutylammonium bromide (0.010 g, 0.03 mmol) in water (10 ml) and the mixture is stirred at room temperature for 3 h. The mixture is diluted with chloroform (20 ml), the organic layer separated, dried with anhydrous sodium sulphate, and evaporated to give the crude product which is recrystallized from ethanol; yield: 0.40 g (89%); m.p. 140–141 °C (Lit.[6] m.p. 142 °C).

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Table. Aryl Imidates **3**, Diaroylamides **5**, and 4-Chlorophenyl *N*-Phenylbenzimidothioate (**7**)

Product	R^1	Ar or R^2	Yield [%]	m.p.	Molecular formula[a] or Lit. m.p.	
3a	C_6H_5	3-O_2N–C_6H_4	88	83–83.5 °C	$C_{19}H_{14}N_2O_3$	(318.3)
3b	C_6H_5	4-F–C_6H_4	87	91.5–92.5 °C	$C_{19}H_{14}FNO$	(291.3)
3c	C_6H_5	4-Cl–C_6H_4	83	91.5–92.5 °C	92–93 °C[8]	
3d	C_6H_5	4-H_3COOC–C_6H_4	91	109–110 °C	108–109 °C[9]	
3e	CH_3	2-naphthyl	80	62–63 °C	$C_{18}H_{15}NO$	(261.3)
5a	C_6H_5	C_6H_5	91	160–160.5 °C	161–162 °C[7]	
5b	C_6H_5	3-Br–C_6H_4	86	140–141 °C	141 °C[10]	
5c	C_6H_5	4-O_2N–C_6H_4	89	177–178 °C	176 °C[10]	
5d	C_6H_5	3-O_2N–C_6H_4	89	140–141 °C	142 °C[6]	
5e	CH_3	C_6H_5	80	95.5–96.5 °C	94–95 °C[6]	
7	C_6H_5	4-Cl–C_6H_4	45	76.5–77 °C	$C_{19}H_{14}ClNS$	(323.8)

[a] All new compounds gave satisfactory microanalyses (C ±0.36, H ±0.10, N ±0.29).

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