The Synthesis of *N*-Alkyl-*N*-aroylaminocarbonyl Isocyanates

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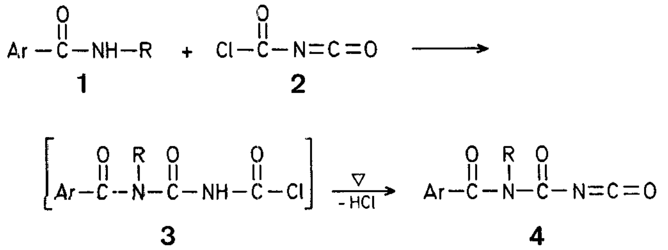
Chlorocarbonyl isocyanate (**2**) has become an important reagent in organic synthesis[1]. Of particular interest is the use of this compound for the synthesis of the new types of isocyanates. Previously, some carbamoyl isocyanates were obtained by treatment of *N*-alkylcarbamates[2], or *N*-alkylamides of phosphoric[3] and sulfonic[4] acids with chlorocarbonyl isocyanate. We have found that alkylamides of aromatic carboxylic acids **1** react with chlorocarbonyl isocyanate (**2**) under mild conditions (in dry benzene at 20 °C) to give at first, probably, unstable adducts **3** which evolve hydrogen chloride at the boiling point of the reaction mixture to give *N*-alkyl-*N*-aroylaminocarbonyl isocyanates **4** in good yields.



The isocyanates **4** are colourless, viscous liquids which are stable in dry air (Table). Their structure is confirmed by microanalysis, I.R., ^{1}H-N.M.R., and mass spectroscopic data.

Alkylamides of aliphatic carboxylic acids also react with chlorocarbonyl isocyanate under similar conditions; however we failed to isolate individual products because the reaction mixture polymerizes on heating or on treatment with triethylamine in the cold. *N*-Alkylamides of trichloro- and trifluoroacetic acid do not react with chlorocarbonyl isocyanate under these conditions.

_N_-Alkyl-_N_-aroylaminocarbonyl Isocyanates 4; General Procedure:
A solution of the carboxylic acid alkylamide **1** (0.03 mol) in dry benzene (25 ml) is added dropwise to a stirred solution of chlorocarbonyl isocyanate (**2**; 3.5 g, 0.033 mol) in benzene (25 ml) at room temperature. The reaction mixture is boiled under reflux for 3–4 h, until the evolution of hydrogen chloride ceases. The solvent is removed and the residue is distilled in vacuo to afford the pure compound **4** (Table).

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Table. *N*-Alkyl-*N*-aroylaminocarbonyl Isocyanates **4** prepared

Product No.	R	Ar	Yield[a] [%]	b.p. [°C]/torr	Molecular formula[b]	I.R. (CCl$_4$) ν [cm^{-1}]	^{1}H-N.M.R. (CCl$_4$/TMS) δ [ppm]	M.S. m/e (M$^+$)
4a	CH$_3$	C$_6$H$_5$	65	86°/0.2	$C_{10}H_8N_2O_3$ (204.2)	2260, 1730, 1690	7.5–8.1 (m, 5H); 3.6 (s, 3H, CH$_3$)	204
4b	*i*-C$_3$H$_7$	C$_6$H$_5$	55	96°/0.2	$C_{12}H_{12}N_2O_3$ (232.2)	2260, 1720, 1700	7.5–8.4 (m, 5H); 4.3–5.0 (m, 1H, CH); 1.73 (d, 6H, J=7 Hz, CH$_3$)	232
4c	CH$_3$	*p*-H$_3$C—C$_6$H$_4$	70	95°/0.2	$C_{11}H_{10}N_2O_3$ (218.2)	2270, 1730, 1690	7.3–8.0 (m, 4H); 3.58 (s, 3H, CH$_3$); 2.74 (s, 3H, CH$_3$)	218
4d	*i*-C$_3$H$_7$	*p*-H$_3$C—C$_6$H$_4$	48	86°/0.08	$C_{13}H_{14}N_2O_3$ (246.3)	2270, 1730, 1690	7.3–8.0 (m, 4H); 4.4–5.0 (m, 1H, CH); 2.71 (s, 3H, CH$_3$); 1.71 (d, 6H, J=7 Hz, CH$_3$)	246
4e	CH$_3$	*p*-Cl—C$_6$H$_4$	60	106°/0.2	$C_{10}H_7ClN_2O_3$ (238.6)	2260, 1730, 1690	7.6–8.0 (m, 4H); 3.61 (s, 3H, CH$_3$)	238
4f	*i*-C$_3$H$_7$	*p*-Cl—C$_6$H$_4$	65	100°/0.1	$C_{12}H_{11}ClN_2O_3$ (266.7)	2260, 1720, 1690	7.6–8.0 (m, 4H); 4.5–5.1 (m, 1H, CH); 1.76 (d, 6H, J=7 Hz, CH$_3$)	266

[a] Yield of pure, isolated product.

[b] All compounds gave satisfactory microanalyses (C ±0.35, H ±0.15, N ±0.2).

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