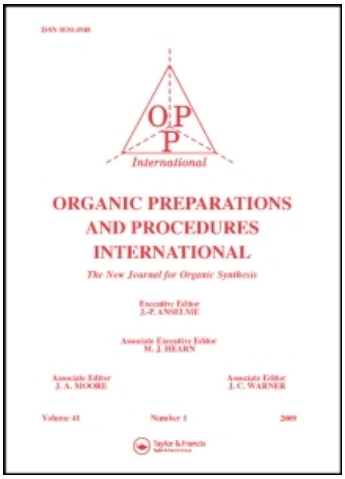

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CHLORINATION OF PYRIDAZINONES WITH CHLOROCARBONYL ISOCYANATE

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ml of hexane. The warm solution (30-35°) was cooled down to -25° for 15 min. to start precipitation and then was left overnight at -15°. The white crystalline solid was collected, washed on the filter with small portions of cold hexane, dried in vacuum (0.3 mm) at room temperature to furnish 26.6 g (71%) of 1, mp. 33-35°.

IR(KBr): 3350, 1689 cm^{-1}; ^{1}H-NMR($CDCl_3$,200 MHz): δ 1.45 (s, 9H, CH_3), 1.68 (small s, traces of 3), 3.57-3.45 (m, 4H, CH_2), 4.95 (broad s, 1H, NH). MS: m/z 226 (22.6%), 224 (22.4%), 170 (82.5%); 168 (68%), 57 (100%).

GC, (Shimadzu, MINI-3,OV-101): 98.6%; (Varian-6500, DB-1): 100%.

Anal. Calcd for $C_7H_{14}BrNO$: C, 37.54; H, 6.30; N, 6.25; Br, 35.65

Found: C, 37.34; H, 6.12; N, 6.11; Br, 35.44

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CHLORINATION OF PYRIDAZINONES WITH CHLOROCARBONYL ISOCYANATE

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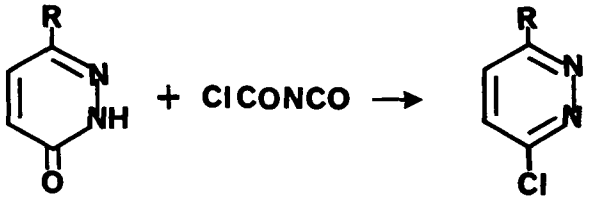
Chlorocarbonyl isocyanate (CCI), a versatile reactive isocyanate with two functional groups has been extensively employed for the synthesis of a wide variety of heterocyclic systems.[1] In view of our earlier observation that chlorosulfonyl isocyanate (CSI) acts as a chlorinating agent with

azinones,[2] it was of interest to study the behavior of CCI towards azinones. Reactions of CCI (1) with 6-aryl-3-(2H)pyridazinones (2)[3a] yielded 6-aryl-3-chloropyridazines (3), thus showing for the first time that CCI may act as a chlorinating agent. The chloropyridazines thus obtained (see Table 1) were shown to be identical with authentic samples,[3b,4,5] by undepressed melting



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points and superimposable IR spectra as well as by accurate mass measurement.

TABLE 1. 6-Aryl-3-chloropyridazines

3	R	Solvent	Temp. (°C)	Time[a] (hrs)	Yield (%)	mp. (°C)	Lit. mp. (°C)
a	C_6H_5	CH_3CN	50-55	4	71	159-160	158-160[3b]
b	$4\text{-}CH_3C_6H_4$	$CHCl_3$	50-55	4	70	151-152	153-154[3b]
c	$4\text{-}CH_3OC_6H_4$	CH_3CN	50-60	4	73	161-162	160[3b]
d	$4\text{-}ClC_6H_4$	$C_2H_2Cl_4$	60-65	4.5	71	196-198	200-201[4]
e	$3,4\text{-}Me_2C_6H_3$	$C_2H_2Cl_4$	60-65	4.5	70	133-134	133-134[5]

a) After carrying the reaction for the time and at the temperature specified, it was allowed to continue at room temperature overnight. Longer reaction time and higher temperature have no significant effect upon the yield.

EXPERIMENTAL SECTION

Melting points were determined with a Buchi 510 melting point apparatus in capillary tubes and are uncorrected. The IR spectra were recorded as potassium bromide pellets on a Perkin-Elmer model 283B spectrophotometer. Mass spectra were obtained on V.G. micromass 7070H mass spectrometer at 70 eV. Accurate mass measurements were carried out at a resolution of 5000 with V.G. data system and PFK was used as reference. Satisfactory microanalysis were obtained for all the compounds synthesized. Chlorocarbonyl isocyanate was obtained from Aldrich Chemical Company Ltd., U.K.

CAUTION! This reagent is corrosive and moisture sensitive.

Typical Procedure.- To 6-phenyl-3-(2H)pyridazinone (2.58 g, 0.015 mol)

dissolved in acetonitrile (35 ml) with heating, was added over a period of 10 min, chlorocarbonyl isocyanate (1.2 ml, 0.015 mol) in acetonitrile (5 ml) at 50-55°. Stirring was continued for 3 hrs at this temperature and overnight at room temperature. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel using chloroform followed by mixtures of chloroform and methanol as eluents. 6-Phenyl-3-chloropyridazine (3a) was obtained by concentration ion of fractions 1 and 2 under reduced pressure and recrystallized from chloroform-ether.

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