Organic Process Research & Development **2003**, *7*, 329−333

Reinvestigation of the Reaction of Trichloroacetyl Chloride and Acrylonitrile in the Preparation of 3,5,6-Trichloropyridin-2-ol

H. Fakhraian,* A. Moghimi, A. Bazaz, H. Hadj-Ghanbary, and M. Sadeghi

Department of Chemistry, Imam Hossein University, Tehran, Iran

Abstract:

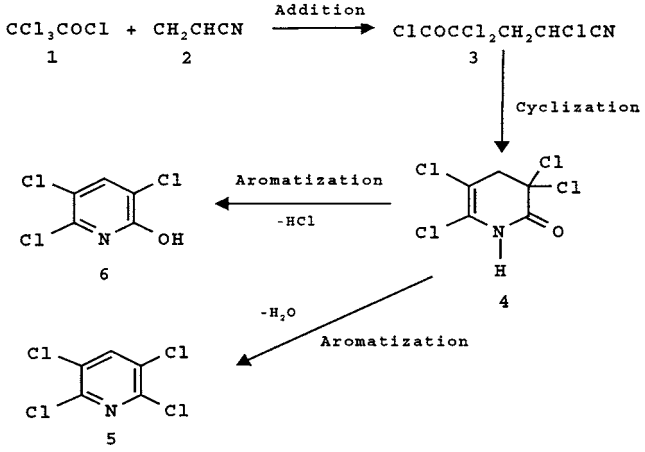
The synthesis of 3,5,6-trichloropyridin-2-ol via the CuCl-catalyzed reaction of trichloroacetyl chloride and acrylonitrile under both pressure and atmospheric conditions and the hydrolysis of the reaction mixture were reinvestigated. The products and byproducts formed in each case, before the hydrolysis step, were characterized, and the factors causing their formation are discussed. It was found that two newly identified byproducts influence the yield of the reaction.

Introduction

3,5,6-Trichloropyridin-2-ol (**6**) is a valuable intermediate for the commercial production of chlorpyrifos (Dursban insecticide) and triclopyr (Garlon herbicide). Different methods for the preparation of this compound have already been reported,[1−11] among which the CuCl-catalyzed addition of trichloroacetyl chloride (**1**) to acrylonitrile (**2**) is the most attractive and well-known method for the large-scale production of this compound.[6−11]

The mechanism of this reaction has been studied, and a three-stepreaction (addition, cyclization, and aromatization (Scheme 1)) has been proposed.[8] 2,2,4-Trichloro-4-cyanobutanoyl chloride (**3**) is produced by the addition of **1** to **2** under atmospheric pressure using a nitrogen stream.[8,11] The cyclization of **3** in the presence of HCl and under pressure conditions has led to 3,3,5,6-tetrachloro-3,4-dihydropyridin-2(1H)-one (**4**) and the hydrolysis of **4** has afforded **6**.[8]

Scheme 1. **Mechanism pathway for the reaction of 1 with 2 proposed by Pew et al.[8] in the preparation of 6**



Nevertheless, the reaction of **1** with **2** and the hydrolysis of the reaction mixture is an attractive method, involving fewer separation and purification steps; Carrying out this reaction in the absence of a nitrogen stream has led directly to **4**, and the aromatization of **4** to **6** is performed using a mineral base (e.g., NaOH).[7,9,10]

The above-mentioned reaction has also been studied under pressure conditions, and co-joint formation of 2,3,5,6-tetrachloropyridine (**5**) and **6** has been observed.[6] The hydrolysis of **5** to afford **6** has been well documented.[5]

Although considerable attention has been paid to the major products formed under different reaction conditions, the nature of the byproducts, as a limiting factor that affects the yield of target product **6**, has not been studied and discussed in detail yet. In this contribution, we propose the mechanism of the reaction of **1** with **2** under both pressure and atmospheric conditions in more detail. Considering the mechanism, we also introduce the optimized conditions to minimize the byproducts.

Results and Discussion

The CuCl-catalyzed reaction of **1** with **2** was performed under both pressure and atmospheric conditions. The reaction mixture components were separated and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (see Experimental Section). In addition to reactant **2**, four products (**3**, **4**, **5**, and **6**) and two byproducts (**7** and **8**) have been recognized, the amounts of which depend on the reaction conditions, as summarized in Scheme 2 and Table 1. The different approaches to convert each of the products **3**, **4**, and **5** to the main product (**6**) are stated above.

* Corresponding author. Fax: +98-7313938. E-mail: fakhraian@yahoo.com.

(1) Rigterink, R. H. U.S. Patent 3,244, 586; *Chem. Abstr.* **1966**, *65*, 681e.
(2) Rigterink, R. H.; Kenega, E. E. *J. Agric. Food Chem.* **1966**, *14*, 4(3), 304−306.
(3) Orth, W. Ger. Offen. DE 3, 308,800; *Chem. Abstr.* **1951**, *45*, 8013f.
(4) Hertog H. J.; de Bruyn, J. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 182−190.
(5) (a) Seitetsu K. Co. Ltd. Jpn. Kokai Tokkyo Koho JP 58 154,561; *Chem. Abstr.* **1984**, *100*, 120891w. (b) Yamagiwa, S.; Takabe, A. Jpn. Kokai Tokkyo Koho JP 62 39,570; *Chem. Abstr.* **1987**, *107*, 58877k. (c) Shishido, S.; Sanada, H.; Noda, S. Jpn. Kokai Tokkyo Koho JP 63 313,771; *Chem. Abstr.* **1989**, *110*, 154165j. (d) Kamei, N. Jpn. Kokai Tokkyo Koho JP 01 68,357; *Chem. Abstr.* **1989**, *111*, 115051v. (e) Kamei, N. Jpn. Kokai Tokkyo Koho JP 01 203,364; *Chem. Abstr.* **1990**, *112*, 55624t. (f) Kamei, N.; Nishiwaki, F. Jpn. Kokai Tokkyo Koho JP 01 203,363; *Chem. Abstr.* **1990**, *112*, 76966w.
(6) Martin, P. Eur. Pat. Appl. 30,214; *Chem. Abstr.* **1981**, *95*, 150459g.
(7) Martinuzzi, E. A.; Colonna, A. O. Braz. Pedido PI BR 87 03,983; *Chem. Abstr.* **1989**, *111*, 97100d.
(8) Pew, G. R. Eur. Pat. Appl. EP 397,281; *Chem. Abstr.* **1991**, *114*, 164019m. Pew, G. R.; Gall, J. A. *J. Org. Chem.* **1994**, *59*, 9(22), 6783−6785.
(9) Xu, D.; Xu, Z.; Dai, J.; Chen, M.; Zhang, M. *Zhejiang Gongye Daxue Xuebao* **1996**, *24(1)*, 16−23; *Chem. Abstr.* **1996**, *125*, 58283k.
(10) Zhang, S.; Cao, R.; Li, G.; Liu, L. *Huaxue Shiji* **1993**, *15(1)*, 54; *Chem. Abstr.* **1993**, 119, 95277h.
(11) Adaway, T. J.; Kershner, L. D. PCT Int. Appl. WO 97 05,112; *Chem. Abstr.* **1997**, 126, 212052p.

10.1021/op025610t CCC: $25.00
Published on Web 04/03/2003

Scheme 2. **Proposed mechanism pathway for the reaction of 1 with 2 in the preparation of 6**

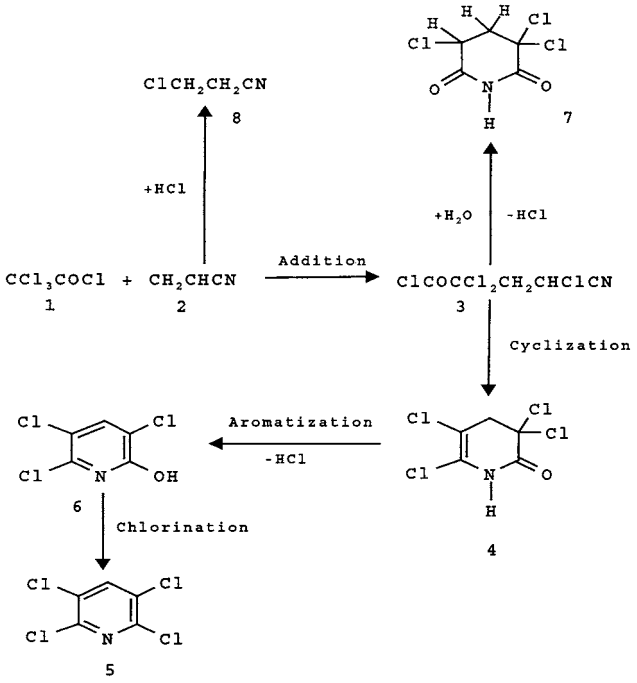


Table 1. **Proportional composition (%)[a] of the reaction mixture under different pressure and atmospheric conditions**

expt	pressure condition (atm)	2:1 molar ratio[b]	temp (°C)	time (h)	2	3	4	5	6	7	8
1	∼6	1:0.9	120−150	6	−	−	21	22	22	13	22
2	∼6	1:1.25	120−150	6	−	−	35	22	3	15	25
3	∼6	1:0.66	150	5	−	−	3	26	29	16	26
4[c]	∼6	1:0.66	150	5	−	−	−	34	−	−	66
5	∼3	1:0.5	110	8	35	−	30	3	5	−	27
6[d]	∼1	1:0.83	80−110	32	25	65	3	−	2	2	3
			110−135	8	12	−	40	17	5	20	6
7[e]	∼1	1:0.83	95−135	20	4	87	9	−	−	−	−
			135−140	4	2	−	66	20	−	10	2

[a] Based on ^{1}H NMR spectroscopy [b] Molar ratio of CuCl:**1** was 0.05 in the following experiments [c] Reaction was done in the presence of $SOCl_2$ as chlorinating agent [d] Reaction was performed during 32 h under nitrogen stream and then continued for 8 h switching off the nitrogen stream [e] Reaction was followed, as in experiment 5, in two steps and in nitrobenzene as solvent

As indicated in Table 1, **8** is one of the major byproducts produced to the highest extent under pressure conditions. It is clear that the starting material **2** is partially consumed via the formation of **8**; thus, the yield of species that can be converted to **6** is decreased. The byproduct **8** is formed by the reaction of **2** with the HCl produced in course of the reaction. Considering the fact that formation of **8** under pressure conditions is remarkable (22%) (Table 1, experiment 1; Figure 1), starting material **2** has to be used in excess to compensate its partial loss during the reaction. However, the large excess of **2** is not recommended because it induces the explosive property of the reaction mixture under pressure conditions if the stirring and temperature of the reaction mixture are not properly controlled. This situation occurred above 110 °C where a large amount of **4** was transformed to **5** and **6** (Table 1, experiments 3 and 5). The pressure, the

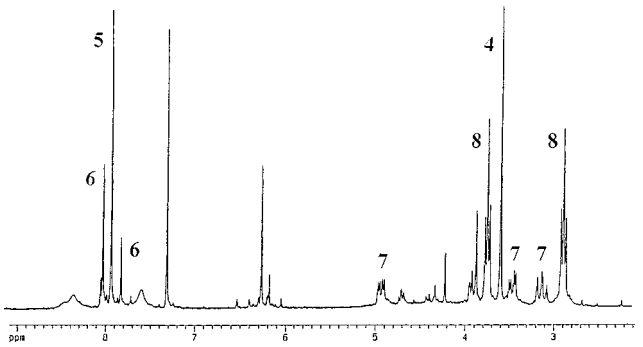


Figure 1. **^{1}H NMR spectrum (in $CDCl_3$) of the reaction mixture in pressure conditions (∼6 atm) (experiment 1, Table 1).**

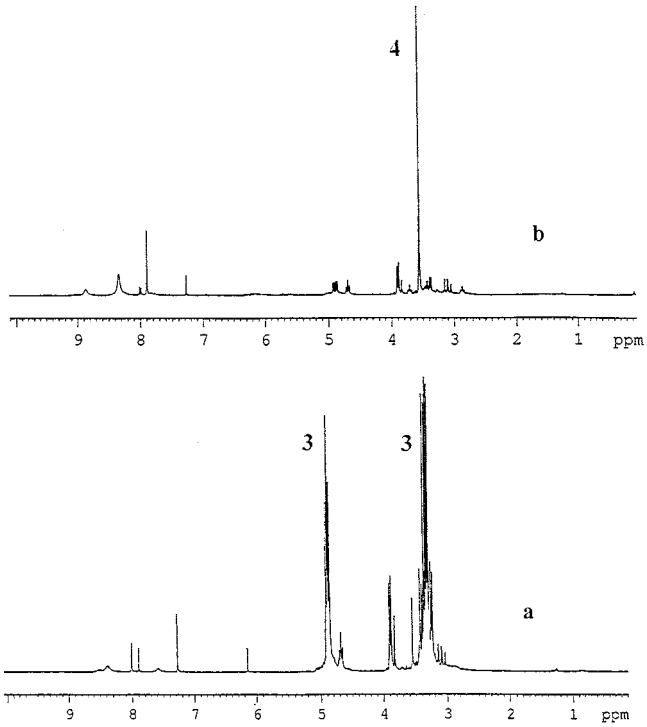


Figure 2. **^{1}H NMR spectrum (in $CDCl_3$) of the reaction mixture in atmospheric pressure conditions (∼1 atm). (a) After 32 h under the nitrogen stream; (b) 8 h after switching off the nitrogen stream (experiment 5, Table 1).**

conversion rate, and the formation of **4**, **5**, and **6** considerably varied with the temperature. After 5 h at 150 °C, the pressure attained was 6 atm, the conversion was completed, and the products were **5** and **6** (Table 1, experiment 3), whereas after 8 h at 110 °C, the pressure, the conversion, and the main product formed were 3 atm, 65%, and **4**, respectively.

The solventless reaction of **1** with **2** under atmospheric pressure without the continuous purging of nitrogen gas, led to **4** and **8**. Performing the above reaction under a nitrogen stream (lasted for 32 h) caused the reflux temperature to increase from 80 to 110 °C. At this point, 75% of **2** was converted, and the main product was **3**. (Table 1, experiment 6; Figure 2a). Carrying out the reaction under a nitrogen stream and expelling HCl formed in course of the reaction resulted in minimizing the formation of **8** and detaining the reaction to the first step since the cyclization step (and the formation of **4**) requires HCl.[8] Interestingly, the cyclization

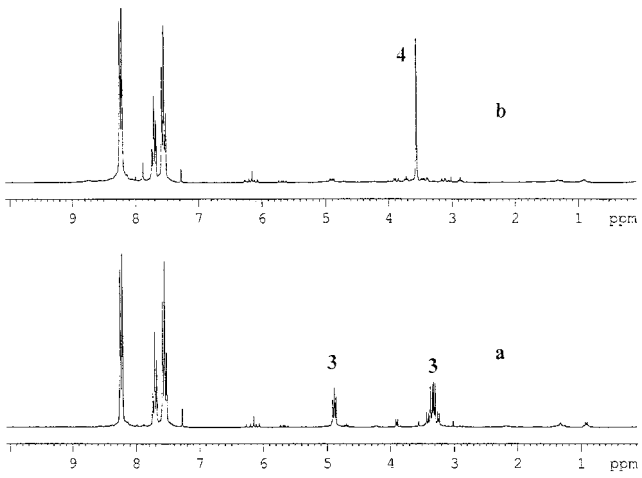


Figure 3. **^{1}H NMR spectrum (in $CDCl_3$) of the reaction mixture in atmospheric pressure conditions (∼1 atm) in nitrobenzene (a) After 20 h under the nitrogen stream; (b) 4 h after the nitrogen stream is switched off (experiment 6, Table 1).**

step was immediately initiated and occurred while the nitrogen stream was stopped for 8 h (Table 1, experiment 6; Figure 2b). In this elapsed time, the reflux temperature was increased to 135 °C. The large excess of **2** is not recommended in a solventless condition because it controls the reflux temperature and reduces the rate of the reaction.

The reaction was also carried out in nitrobenzene as a high-boiling-point solvent. The reflux temperature was started at 95 °C and reached 135 °C after 20 h with 96% conversion of **2** (Table 1, experiment 7; Figure 3a). By switching off the nitrogen stream and continuing the reaction for another 4 h, the cyclization reaction took place, and **3** was totally transformed to **4**, **5**, and **7** (Table 1, experiment 7; Figure 3b). The rate of the conversion was increased in nitrobenzene because the reflux temperature moved up faster than in the absence of nitrobenzene. This experiment did not attain the results emphasized in the literature.[7] It is presumed that the reaction has been done under pressure conditions in the corresponding work because the elevation of temperature to 140 °C in 4 h is impossible under atmospheric pressure. In this condition, as in the solventless experiment, the formation of **8** was minimized. However, despite the better yield of **4** and **5** and the minor formation of **7** and **8**, the final product—after hydrolysis of the reaction mixture under atmospheric pressure—was an oily solid, the separation of which was difficult. The separation of **5** was also complicated.

Cyclic 3,3,5 trichloropiperidine-2,6-dione (**7**) was the second byproduct formed via the hydrolysis of 3.[11] It decreased the yield of the reactions performed under both pressure and atmospheric conditions (10−20%). Water necessary to the hydrolysis of **3** is provided by the transformation of **6** to **5**. The lack of **7** in 110 °C and ∼3 atm, where **5** and **6** are absent (Table 1, experiment 5), is to be noted in this context.

The two byproducts **7** and **8** were separated, and their physicochemical parameters were in accordance with those reported in the literature[11,13] (see Experimental Section). Treating the reaction mixture with $CHCl_3$ causes the separation of **7**. Effectively, all of the mixture components were readily soluble in $CHCl_3$ except for **7** and the catalyst. The ^{1}H NMR spectrum of **7** shows three distinct quartets and one broad singlet associated with C−H and N−H protons, respectively. The ^{1}H and ^{13}C NMR chemical shifts and the coupling constant data of **7** and **8** have been given in the Table 2, and the ^{1}H NMR spectrum of the pure isolated **7**, in Figure 4.

The compound **5** was formed under both conditions (pressure and atmospheric) to the same extent (17−22%). We believe that the compound **5** is formed by chlorination of **6** under both conditions via the starting material **1** as the chlorinating agent. This was confirmed when we used **1** in excess under pressure conditions (Table 1, experiment 2), where the percentage of **6** in the reaction mixture was decreased. To further confirm the production of **5** from **6** under the experimental conditions, an additional experiment was designed and performed. It was found that chlorination of **6** by **1** in $CHCl_3$ at reflux temperature occurs. In the presence of $SOCl_2$ as chlorinating agent, **5** and **8** are the only components of the reaction mixture (Table 1, experiment 4). It seems that strong chlorinating agent can transform both **6** and **7** to **5** and favor the formation of **8**. This is interesting if the production of **5** in lower yield is desired.

The hydrolysis of **5** to **6** does not occur as readily as that of **4** to **6** and requires critical conditions.[5] The hydrolysis of the reaction mixture under pressure (∼2 atm) at 150 °C and after 2 h resulted in complete transformation of **4** and **5** to **6**. Under atmospheric pressure and reflux temperature during a moderate time interval (1−2 h), the transformation of **4** to **6** took place, while **5** was remained unaltered (see Experimental Section).

Summary

In summary, we have identified two principal byproducts (**7** and **8**) formed in the course of a three-step reaction of **1** and **2** to produce **6**. Under atmospheric pressure (∼1 atm) and nitrogen stream, the formation of **8** is minimized; however, under pressure (∼6 atm), **8** is one of the major constituents of the reaction mixture. The compound **7** is formed approximately to the same extent in the both conditions. The aromatization of **4** to **6** liberates HCl and causes the formation of **8** by the hydrochlorination of **2** in pressure conditions. This reaction does not take place in atmospheric pressure conditions when a nitrogen stream passes through the reaction mixture. The chlorination of **6**, i.e., its transformation to **5**, occurs by **1** in both conditions and causes the formation of H_2O that hydrolyzes **3** to **7**. Thus, the reaction must be controlled in such a way that **1** is totally eliminated in the reaction medium before the cyclization and aromatization steps, i.e., the formation of **4** and **6**, occur. With nitrobenzene as solvent and under atmospheric pressure, the formation of **4** is favored and that of **7** is minimized.

(12) Martin, P.; Bellus, D. Eur. Pat. Appl. 30,215; *Chem. Abstr.* **1981**, *95*, 150458f.
(13) Iddon, B. *Tetrahedron Lett.* **1976**, *8*, 627−630.

Table 2. **^{13}C nd ^{1}H NMR Chemical Shift and the *J* values in 7 and 8**

compound	^{13}C NMR δ (ppm)	^{1}H NMR δ, *J* (ppm, Hz)
2-chloropropionitrile (**8**)	22, 38, 116	2.8 (t, 6.6), 3.6 (t, 6.6)
3,3,5-trichloropiperidine-2,6-dione (**7**)	47, 50, 51, 163, 166	3.07 (q, 12.1,14.5), 3.40 (q, 5.5, 14.5), 4.90 (q, 5.5, 12.1). 8.3 (s)

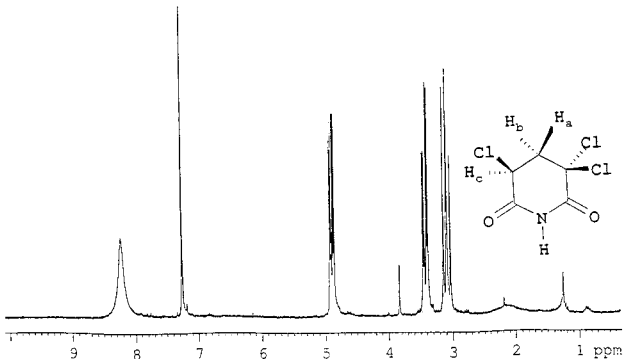


Figure 4. **^{1}H NMR spectrum (in $CDCl_3$) of 3,3,5-trichloropiperidine-2,6-dione (7).**

Experimental Section

General Procedures. NMR spectra were recorded on a Bruker DPX-250 instrument (250 MHz for ^{1}H and 62.5 MHz for ^{13}C), and $CDCl_3$ was used as solvent; chemical shifts were reported in δ (ppm) from TMS (^{1}H and ^{13}C) that was used as internal standard. IR spectra were recorded on a Perkin-Elmer 783 instrument using KBr pellet (selected data given). Melting points were obtained on a Mettler FP61 apparatus. Elemental analysis was performed using a Carlo Erba analytical gas chromatograph.

Reaction of 1 with 2 under Atmospheric Pressure Conditions (~1 atm). Trichloroacetyl chloride (363.6 g, 2.0 mol), acrylonitrile (127.2 g, 2.4 mol), and anhydrous CuCl (10 g, 0.1 mol) were refluxed under nitrogen atmosphere while stirring. The reflux temperature for the reaction mixture was started at ~80 °C and was increased to 110 °C after 32 h. The nitrogen stream was then stopped, and heating the reaction mixture was continued for 8 h to reach the reflux temperature, 130 °C. Yield of the crude product, consisting essentially of **2**, **4**, **5,** and **7**, was 415 g. Then 600 mL of 48% aqueous NaOH solution was added slowly while stirring and controlling the temperature of the mixture at 30−40 °C. Afterward, the hydrolysis of the reaction mixture was performed at reflux temperature for 2 h. The solution was filtered, and the solid mixture of **5** and sodium salt of **6** were dissolved in 500 mL of $CHCl_3$. The solid sodium salt of **6** was filtered, washed with 100 mL of $CHCl_3$, and dissolved in 5 L of hot H_2O. The solution was acidified to pH = 4 at 25 °C, and the precipitate (**6**) was filtrated and dried; 141 g of **6** (0.71 mol) was obtained. The evaporation of $CHCl_3$ of the precedent filtrate and drying the solid afforded 84 g of **5** (0.39 mol). The total yield of **5** and **6** was 55%.

Reaction of 1 with 2 under Atmospheric Pressure Conditions (~1 atm) in Nitrobenzene. Trichloroacetyl chloride (36.4 g, 0.2 mol), acrylonitrile (12.7 g, 0.24 mol) and anhydrous CuCl (1 g, 0.01 mol) were mixed with 20.6 mL of nitrobenzene (24.6 g, 0.1 mol) and refluxed under nitrogen atmosphere, while stirring. The reflux temperature for the reaction mixture was started at ~90 °C and was increased to 135 °C after 20 h. The nitrogen stream was then stopped, and heating the reaction mixture was continued for 4 h. Yield of the crude product, consisting essentially of **4**, **5**, and **7**, was 52.5 g. Then 60 mL of 48% aqueous NaOH solution was added slowly (in 20 min) with stirring while controlling the temperature of the mixture at 30−40 °C. Afterward, the hydrolysis of the reaction mixture was performed at reflux temperature for 2 h. The solution was filtered, and the oily solid sodium salt of **6** was washed with 50 mL of $CHCl_3$. The resulting oily solid was dissolved in 3 L of hot water. The solution was acidified to pH = 4 at 25 °C, and the precipitate (**6**) was filtrated and dried.

Reaction of 1 with 2 under Pressure Conditions (~6 atm). Trichloroacetyl chloride (146 g, 0.8 mol), acrylonitrile (51 g, 0.96 mol) and anhydrous CuCl (4 g, 0.04 mol) were heated in a 250-mL glass autoclave equipped with a magnetic stirrer and pressure gauge. The mixture was stirred for 3 h in an oil bath at 120 °C. The initial pressure was 1.5 atm which then reached 3 atm after 1 h. Then the reaction was continued for 3 h at 150 °C, during which the pressure was augmented to 6 atm. After the reaction was stopped and the mixture was cooled, the yield of the crude product, consisting essentially of **4**, **5**, **6**, **7**, and **8**, was 182 g. Then 300 mL of 48% aqueous NaOH solution was added slowly while controlling the temperature of the mixture in the range 30−40 °C, after which the hydrolysis reaction was performed at 150 °C under 2 atm during 2 h. Filtration of the reaction mixture and washing the solid with 100 mL of cold H_2O gave the sodium salt of **6** that was dissolved in 3 L of hot H_2O. Then the solution was acidified to pH = 4 at 25 °C. The precipitate **6** was filtered and dried to afford 97 g (0.49 mol, 61%) of light yellow crystals of **6** (specifications as in the following section).

Separation and Purification of Mixture Constituents. To characterize each of the components, the following separation and purification steps were applied to the reaction mixture obtained as above before its hydrolysis.

(1) The crude product obtained under pressure conditions was vacuum-distilled at 95 °C and 50 mmHg to obtain **8**. ^{1}H NMR ($CDCl_3$): 2.8 (t, *J* = 6.6 Hz), 3.6 (t, *J* = 6.6 Hz) ppm (in agreement with lit.[14]), ^{13}C NMR ($CDCl_3$): 22, 38, 116 ppm.

The vacuum distillation at 90 °C and 5 mmHg of the crude product obtained under atmospheric pressure conditions and

(14) Hirst, R. C. *J. Chem. Phys.* **1964**, *40(7)*, 1909−1919.

nitrogen stream before cyclization, afforded **3**. ^{1}H NMR ($CDCl_3$): 3.29 (q, J = 6, 15.5 Hz, 1H, CH_2), 3.40 (q, J = 7.5, 15.5 Hz, 1H, CH_2), 4.91 (t, J = 6, 7.5 Hz, 1H, CHCl) ppm, ^{13}C NMR ($CDCl_3$): 37,49,84,115,167 ppm.

(2) $CHCl_3$ was added to the reaction mixture obtained after the first step of the separation and purification procedure, and the precipitate **7** and the catalyst were filtered off. The filtrate was used for the next step, and the solid obtained was dissolved in acetone to separate **7** from the catalyst. By evaporation of the solvent, the cyclic compound **7** (i.e., 3,3,5-trichloropiperidine-2(1H)-one) was obtained. ^{1}H NMR ($CDCl_3$): 3.07 (q, J = 12.1, 14.5 Hz, 1H, CH_2), 3.40 (q, J = 5.5, 14.5 Hz, 1H, CH_2), 4.90 (q, J = 5.5, 12.1 Hz, 1H, CHCl), 8.3 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$): 47, 50, 51, 163, 166 ppm, mp = 156−157 °C (lit.[11] 158−159 °C). Anal. Calcd for $C_5H_6Cl_3NO_2$: C, 27.71; H, 1.85; N, 6.47. Found: C, 27.48; H, 1.85; N, 6.59. IR (KBr pellet); 438(m), 557(m), 636(m), 684(s), 789(s), 925(m), 1016(m), 1065(m), 1103(m), 1179(s), 1232(vs), 1310(m), 1332(m), 1419(m), 1731(vs), 2825(w), 2985(m), 3120(m), 3225(s), 3430(w) cm^{-1}.

(3) The 20% Na_2CO_3 solution was added to the filtrate of the second step. The precipitated sodium salt of **6** was separated and dissolved in water. After the acidification of the solution to pH = 4 at 25 °C, the compound **6** was precipitated. It was filtrated and dried. ^{1}H NMR ($CDCl_3$): 7.8 (s, 1H, CH), 10.6 (s, 1H, OH) ppm. ^{13}C NMR (DMSO): 116, 120, 141, 143, 158 ppm (in agreement with lit.[10]). mp = 171−2 °C (lit.[6] 171−172 °C). IR (KBr pellet); 541(w), 688(m), 750(m), 820(w), 893(w), 893(w), 954(w), 1021(w), 1078(s), 1155(m), 1211(s), 1273(w), 1315(s), 1382(m), 1452-(vs), (1534(w), 1569(s), 1640(w), 2560(m), 2725(m), 2905-(m), 3040(m) cm^{-1}.

(4) The solvent of the organic phase of the precedent step (CH_3Cl) was evaporated, and the residue was treated and extracted with hot *n*-hexane. The solution was allowed to cool. The crystalline product **4** was filtrated and dried. ^{1}H NMR ($CDCl_3$): 3.55 (s, 2H, CH_2), 8.45 (s, 1H, NH) ppm (in agreement with lit.[8]). ^{13}C NMR ($CDCl_3$): 50,79,108,-122,162 ppm. Mp = 136−137 °C (lit.[8] 126−127 °C). IR (KBr pellet); 540(w), 583(s), 666(m), 697(s), 757(s), 790-(s), 908(m), 941(s), 1023(s), 1074(w), 1103(w), 1186(s), 1210(s), 1276(s), 1338(s), 1400(m), 1450(s), 1577(m), 1697-(vs), 2905(s), 3010(s), 3175(s) cm^{-1}.

(5) The solvent of the filtrate of the precedent step was evaporated and the compound **5** was obtained as the last component of the mixture. ^{1}H NMR ($CDCl_3$): 7.9 (s) ppm. ^{13}C NMR ($CDCl_3$): 130,140,146 ppm (in agreement with lit.[13]). Mp = 90−91 °C (lit.[6,12] 90−91 °C). IR (KBr pellet); 495(w), 637(s), 671(m), 708(w), 918(m), 1061(s), 1161(s), 1219(m), 1323(m), 1361(vs), 1387(s), 1506(m), 1719(m), 3010(m) cm^{-1}.

Acknowledgment

Supported by the Iranian Ministry of Industry (Grant No. 78210111076)

Received for review November 18, 2002.

OP025610T