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The Formation of Benzoyl Chlorides from 1,2-Dibenzoylhydrazines or Dibenzoyldiimides

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The reaction of acid hydrazide with chlorine was reported by Carpino.[1,2] He obtained acid chlorides in good yields from the corresponding hydrazides by successive treatments with hydrogen chloride and chlorine. Later, Kissinger and Ungnade showed that the prior conversion of acid hydrazide to the hydrochloride was not necessary.[3]

The pathway of the reaction was proposed by Carpino to be as in Scheme (1).[2] This mechanism appears to be

$$\text{R-CONHNH}_2 \xrightarrow{\text{HCl}} \text{R-CONH}\overset{+}{\text{N}}\text{H}_3\text{Cl}^- \xrightarrow{\text{Cl}_2}$$

$$[\text{R-CO-N=N-Cl}] \xrightarrow{-\text{N}_2} \text{R-COCl} \qquad (1)$$

reasonable for his reaction conditions. However, in the cases of no concomitant addition of hydrogen chloride (Kissinger's conditions), the reaction seems to proceed not solely through the above pathway (1).

In order to clarify the reaction pathways, we first isolated the intermediates under Kissinger's conditions, using benzoylhydrazine as a representative acid hydrazide.

When benzoylhydrazine was treated with chlorine in nitromethane without prior conversion to the hydrochloride, large amounts of white precipitates appeared at the initial stage of the reaction. These precipitates completely disappeared upon the further introduction of chlorine to give benzoyl chloride in a good yield (78%). The precipitates were identified as a mixture of benzoylhydrazine hydrochloride and1,2-dibenzoylhydrazine (mol ratio: *ca.* 4: 1).

On the other hand, no 1,2-dibenzoylhydrazine was detected at any stage of the reaction under Carpino's conditions.

These results indicate that benzoylhydrazine hydrochloride and 1,2-dibenzoylhydrazine may both be precursors of benzoyl chloride under Kissinger's conditions. This was supported by the results of the reaction of pure 1,2-dibenzoylhydrazine with excess chlorine in nitromethane or dichloromethane; benzoyl chloride was obtained in yields of 76 and 82% in the respective solvents.

Further, several 1,2-bis(substituted benzoyl)hydrazines were allowed to react with chlorine. Table 1 shows the yields of the corresponding chlorides obtained. In the cases of *m*-chloro and *p*-chloro derivatives, the reaction rates were fairly slow, and the chlorides were scarcely obtained.

It is well known that 1,2-diaroylhydrazine is oxidized by halogen to afford diaroyldiimide.[4,5] This suggests that dibenzoyldiimide is also the precursor of benzoyl chloride. Thus, we treated dibenzoyldiimide with chlorine in the same solvents as in the cases of the preceding dibenzoylhydrazines. The reaction proceeded quite smoothly at room temperature. The yields of benzoyl chloride are also shown in Table 1, along with those of other chlorides.

Table 1. Yields of benzoyl chlorides

X	X-C$_6$H$_4$-CONH-NHCO-C$_6$H$_4$-X		X-C$_6$H$_4$-CON=NCO-C$_6$H$_4$-X	
Solvent	CH_3NO_2	CH_2Cl_2	CH_3NO_2	CH_2Cl_2
H	76%	82%[a]	79%	89%
p-CH_3O	87[c]	49[b]+44[c]	11[b]+81[c]	93[b]
p-CH_3	82	87[a]	86	91
o-CH_3	81	90	81	90
o-Cl	79	88	—	—

a) The reaction time was 10—30 hr at room temperature.
b) *p*-Anisoyl chloride.
c) 3-Chloro-4-methoxybenzoyl chloride.

These results lead to the conclusion that acid chloride is formed through both the pathways, (1) and (2), under Kissinger's conditions.[6]

$$2\ \text{R-CONHNH}_2 \xrightarrow{\text{Cl}_2} \text{R-CONHNHCO-R} \xrightarrow{\text{Cl}_2}$$

$$\text{R-CO-N=N-CO-R} \xrightarrow{\text{Cl}_2} 2\ \text{R-COCl} \qquad (2)$$

Experimental

Isolation of Intermediates. Into a solution of 3.91 g of benzoylhydrazine in 120 m*l* of anhydrous nitromethane, dry chlorine gas was passed at about 0.5 m*l*/sec, while stirring was continued for 5 min. The white precipitates thus formed were collected, washed with nitromethane, and dried. This material (1.99 g) was then triturated with 40 m*l* of water; a subsequent filtration left a colorless powder I (0.43 g; mp 238—240°C). The filtrate was evaporated to afford colorless crystals, II (1.50 g, mp 192—194°C (decomp.)).

1) L. A. Carpino, *Chem. Ind.* (London), 123 (1956).
2) L. A. Carpino, *J. Amer. Chem. Soc.*, **79**, 96 (1957).
3) L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **24**, 1244 (1959).
4) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. B. Benjamin, Inc., New York (1966), p. 119.
5) a) R. Stollé and A. Benrath, *Ber.*, **33**, 1770 (1900); b) R. Stollé and A. Benrath, *J. Prakt. Chem.*, [ii], **70**, 263 (1900); c) E. Mohr, *ibid.*, [ii], **70**, 281 (1904); d) R. Stollé, *Ber.*, **45**, 245 (1912); e) L. Horner and W. Naumann, *Ann. Chem.*, **587**, 93 (1954).
6) Dibenzoyldiimide could not be isolated under these reaction conditions. However, we observed that reddish orange color, which was perhaps due to dibenzoyldiimide being formed, appeared in the course of the reaction, and that this color faded just when the reaction was completed.

Table 2. 1,2-Bis(substituted benzoyl)hydrazines

Subst	Mp °C	Analysis (Calcd)			
		C%	H%	N%	Cl%
o-CH_3	219—220	71.82	6.00	10.44	
		(71.62)	(6.01)	(10.44)	
o-Cl	219—221	54.27	3.27	8.79	22.98
		(54.39)	(3.26)	(9.06)	(22.94)
m-Cl	272—274	54.47	3.20	9.23	23.22
		(54.39)	(3.26)	(9.06)	(22.94)

The substances (I and II) separated above were identified as 1,2-dibenzoylhydrazine and benzoylhydrazine hydrochloride respectively by comparing their infrared spectra with those of authentic samples.

1,2-Dibenzoylhydrazines. These were prepared by the usual method.[7] The melting points and analytical data for the new hydrazines are listed in Table 2.

Dibenzoyldiimides. The general procedures were as follows. 1,2-Dibenzoylhydrazine (0.20 mol) was saturated in dimethylformamide. Bromine (48 g, 0.30 mol) was added dropwise into this solution with vigorous stirring for 15 min. After the addition of bromine, stirring was continued for 2 hr, and then the reaction mixture was poured into *ca.* 3 *l* of ice water. The precipitated solid was collected, washed with water, and dried *in vacuo* at 50—60°C. The yield of the crude product was 87—94%. This crude diimide was recrystallized from *n*-hexane-benzene (2: 1).

The melting points and analytical data for bis(substituted benzoyl)diimides are shown in Table 3.

The Reaction of 1,2-Dibenzoylhydrazine with Chlorine. 1,2-Dibenzoylhydrazine (6—8 g) was suspended in 50 m*l* of nitromethane or dichloromethane. Chlorine gas was passed slowly into this suspension at room temperature until the dibenzoylhydrazine had been completely dissolved. This required 1—5 hr. The solvent was then removed by rotary evaporation, and the liquid was distilled under reduced pressure.

The benzoyl chlorides obtained were identified by comparing their infrared spectra with those of authentic samples.

The Reaction of Dibenzoyldiimides with Chlorine. Dibenzoyldiimides were treated with chlorine under the same conditions as in the cases of the preceding dibenzoylhydrazine. The reactions were completed within 30 min.

Table 3. Bis(substituted benzoyl)diimides

Subst	Mp °C (lit)	Analysis (Calcd)		
		C%	H%	N%
o-CH_3	106—107	72.16	5.19	10.57
		(72.17)	(5.30)	(10.52)
p-CH_3O	136—137	64.62	4.72	9.40
	(131.5—132.0) [b]	(64.42)	(4.73)	(9.39)
p-CH_3	120—121	71.93	5.19	10.65
	(118) [a]	(72.17)	(5.30)	(10.52)
H	119—121	70.36	4.02	11.78
	(119.5—121.5) [b]	(70.53)	(4.23)	(11.81)

a) Ref. 5e
b) Ref. 8

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7) H. H. Hatt, "Organic Syntheses," Coll. Vol. II, p. 208 (1966).

8) J. E. Leffler and W. B. Bond, *J. Amer. Chem. Soc.*, **78**, 335 (1956).