bottle for 8 hr. After cooling, the precipitate was removed, washed with water, dried, and recrystallized from ethanol–acetone. The product, N,N′-dibenzenesulfonyl-N-ethoxycarbonylmethyl-*o*-phenylenediamine (XVI), was obtained in 63.2% yield, m.p. 186–188°; $\nu_{\max}^{\mathrm{KBr}}$ 3220 (m), 1733 (s) (COO), 1343 (s) (SO_2N), 1200 (s), and 1160 (s) (SO_2N) cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{22}N_2O_6S_2$: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.70; H, 4.72; N, 5.76; S, 13.82.

The filtrate from above was evaporated to dryness and the residue was recrystallized from acetone to give a small amount of ethyl 2-benzimidazolecarboxylate. It was then recrystallized from acetone and ligroin, m.p. 225–226° dec.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.03; H, 5.16; N, 14.62.

The infrared spectrum was identical with that of a sample prepared by the method of Copeland and Day.[9]

Conversion of N,N′-Dibenzenesulfonyl-N-ethoxycarbonylmethyl-*o*-phenylenediamine (XVI) to Ethyl 2-Benzimidazolecarboxylate (XVII).—XVI (2.37 g.) was suspended in 50 ml. of dry tetrahydrofuran. Sodium (0.5 g.) was dissolved in 25 ml. of dry ethanol and added to the above mixture. Everything went into solution. This solution was heated at 100° in a pressure bottle for 1 day. On cooling, 1 g. of material precipitated which has not been identified up to now. The filtrate was evaporated to dryness and the residue was extracted with acetone. The residue proved to be sodium sulfinate. The acetone extract was then evaporated and the residue was extracted with a mixture of acetone and ligroin and filtered. Evaporation of the filtrate gave XVII. It was recrystallized from acetone–ligroin, yield 0.45 g. (47%), m.p. 224–225° dec. Comparison of its melting point and infrared spectra with that of an authentic sample established its identity.

Reactions Catalyzed By Potassium Fluoride. IV. The Reaction of N-Chlorobenzamide with Potassium Fluoride

LEON RAND AND RICHARD J. DOLINSKI[1]

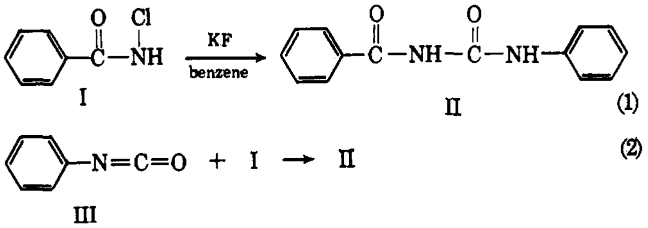
Department of Chemistry, University of Detroit, Detroit, Michigan

Received July 27, 1964

Potassium fluoride has been shown to convert N-chlorobenzamide into N-benzoyl-N′-phenylurea. Initial proton abstraction by the fluoride followed by a Hofmann-type rearrangement gives phenyl isocyanate. Addition of a second mole of the amide to the isocyanate with subsequent hydrolysis yields the product.

Potassium fluoride has been reported to catalyze several reactions. These include the decarboxylation of adipic and 2,2,5,5-tetramethyladipic acids to the corresponding cyclopentanones,[2] the synthesis of 1,2,3,4,5,6-hexaphenylpentalene through the Michael addition of 1,2,3-triphenyl-1,3-cyclopentadiene to 1,2,3-triphenyl-2-propen-1-one,[3] the decarboxylation of certain acids,[4] and various Knoevenagel reactions.[5-7] In addition, a preliminary communication[8] reported that anhydrous potassium fluoride functions as a base in the Hofmann reaction converting N-chlorobenzamide to phenyl isocyanate. This paper describes the mechanism of that reaction and the subsequent formation of N-benzoyl-N′-phenylurea.

When dry N-chlorobenzamide (I) was refluxed in dry benzene with anhydrous potassium fluoride, N-benzoyl-N′-phenylurea (II) was obtained in high yield. The amount of II formed was found to depend upon the concentration of potassium fluoride, 2 equiv. of I reacting with 1 equiv. of the fluoride. Severe etching of the reaction flask was noted indicating the formation of hydrogen fluoride. This is in contrast with the results obtained in the Knoevenagel reaction where it was shown[6] that an equimolar amount of the catalyst was not necessary although a practical lower limit to the concentration that could be used was reached. In this reaction, potassium fluoride presumably abstracts a proton from the active methylene-containing compound with subsequent protonation of the condensed anion to form the alcohol. With N-chlorobenzamide, however, abstraction of the proton by the fluoride results in formation of hydrogen fluoride and potassium chloride. The calculated amount of the chloride was realized from an alkali extract of the reaction mixture. Alternatively, II was obtained in high yield when equimolar amounts of I and phenyl isocyanate were reacted. No reaction occurred when benzamide was refluxed in benzene with potassium fluoride.[9]



I
II
(1)
(2)
III

These observations were taken as evidence for an initial Hofmann rearrangement of 1 mole of N-chlorobenzamide (I) to form the isocyanate. Addition of the second mole of N-chlorobenzamide to phenyl isocyanate followed by hydrolysis yields the product (II). However, on the basis of these considerations, two mechanisms can account for the formation of III. In order to differentiate between reactions 3 and 4, N-chloro-N-methylbenzamide (IV) and potassium fluoride were refluxed in benzene. The fluoride and unchanged IV were recovered quantitatively. Also, when cesium fluoride, which was shown to be a more effective catalyst in the

---

(1) Ethyl Research Fellow, 1962–1964.

(2) L. Rand, W. Wagner, P. O. Warner, and L. R. Kovac, *J. Org. Chem.*, **27**, 1034 (1962).

(3) E. Le Goff, *J. Am. Chem. Soc.*, **84**, 3975 (1962).

(4) A. N. Nesmeyanov, K. A. Pecherskaya, and G. Y. Uretskaya, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 240 (1948).

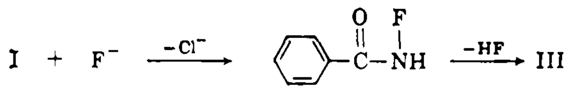
(5) (a) H. Baba, H. Midorikawa, and S. Aoyama, *J. Sci. Res. Inst.* (Tokyo), **52**, 99 (1958); (b) H. Igarashi, H. Midorikawa, and S. Aoyama, *ibid.*, **52**, 105 (1958); (c) A. Sakurai, H. Midorikawa, and S. Aoyama, *ibid.*, **52**, 112 (1958); (d) H. Yasuda, H. Midorikawa, and S. Aoyama, *ibid.*, **53**, 19 (1959); (e) A. Sakurai, *ibid.*, **53**, 250 (1959).

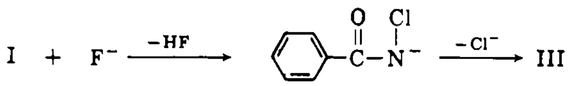
(6) L. Rand, J. V. Swisher, and C. J. Cronin, *J. Org. Chem.*, **27**, 3505 (1962).

(7) R. J. Dolinski, M.S. Thesis, University of Detroit, 1963.

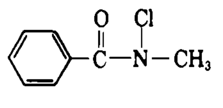
(8) L. Rand, and M. J. Albinak, *J. Org. Chem.*, **25**, 1837 (1960).

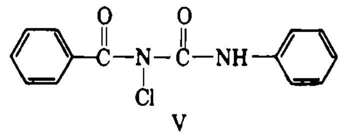
(9) J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 4553 (1960). Trifluoroacetamide and AgF_2 react vigorously to form the corresponding isocyanate by initial hydrogen abstraction and either stepwise abstraction of the second hydrogen or fluorination and concerted loss of HF. Subsequent internal rearrangement of this electron-deficient intermediate yields the isocyanate. However, we have found that potassium fluoride does not react at all with benzamide. This is apparently due to the inability of the weakly acidic N-H bond to react with fluoride.


(3)


(4)

Knoevenagel reaction,[6] was substituted for potassium fluoride, no reaction occurred with IV and the starting materials again were recovered unchanged. This evidence tends to eliminate N-fluorobenzamide as the intermediate since N-fluoro-N-methylbenzamide or its degradation products would have been expected if reaction 3 were the reaction path. On the other hand, the inability of IV to undergo the reaction is best explained by assuming an anion[10] in the transition state which cannot form from the N-methylamide.


IV


V

According to the normal mode of addition of amides to isocyanates,[11,12] N-benzoyl-N-chloro-N′-phenylurea (V) should be anticipated from the reaction between I and III. It would be expected that the hydrolysis of this N-chlorourea to N-benzoyl-N′-phenylurea (II) would be rapid.[13,14] Indeed, when moisture was not excluded from the system, chlorine was evolved *via* hydrolysis of V and the formation of hypochlorous acid.[15] Evidence for the formation of V was obtained by reacting I and III under completely anhydrous conditions. The solid so obtained was hydrolyzed with a dilute sodium hydroxide solution followed by an iodometric determination of hypochlorite[16] whose concentration corresponded to the amount of II isolated after hydrolysis.

It is interesting to note that Stieglitz and Earle[14] reported the isolation of N-benzoyl-N′-(4-chlorophenyl)-urea from the reaction of I and III. However, we have obtained quantitative amounts of II precluding the formation of significant amounts of N-benzoyl-N′-(4-chlorophenyl)urea.

Experimental

Materials.--Potassium fluoride was obtained from Baker and Adamson and cesium fluoride was obtained from American Potash and Chemical Corporation. Phenyl isocyanate was distilled before use and anhydrous benzene was used as a solvent. N-Chlorobenzamide was dried in a heated vacuum desiccator prior to use.

N-Benzoyl-N′-phenylurea (II). A.--A mixture of 15.5 g. (0.1 mole) of N-chlorobenzamide, obtained by the method of Elliot,[17,18] and 2.9 g. (0.05 mole) of potassium fluoride was refluxed in benzene for 12 hr. The yield of product, recrystallized from ethanol-water, was 11.1 g. (95%), m.p. 208-209° (lit.[19] m.p. 206°).

With an excess of N-chlorobenzamide, the yield did not increase but was equal to the concentration of the fluoride.

In order to determine the concentration of chloride formed in the reaction, the product was hydrolyzed with dilute NaOH, filtered, and the filtrate was diluted to exactly 100 ml. A 30-ml. aliquot was treated with H_2O_2 to reduce the hypochlorite to chloride.[20] A gravimetric determination gave 99.57% of the expected chlorine. A second 30-ml. aliquot was then analyzed iodometrically.

Anal. Calcd.: Cl, 50.0; HClO, 50.0. Found: Cl, 51.96; HClO, 47.61.

B.---A mixture of 15.5 g. (0.1 mole) of N-chlorobenzamide and 11.9 g. (0.1 mole) of phenyl isocyanate was refluxed in 100 ml. of benzene for 2 hr. to yield 23.0 g. (96.1%) of N-benzoyl-N′-phenylurea after recrystallization from ethanol.

Attempted Reaction of Benzamide and Potassium Fluoride.--Into a 200-ml. flask equipped with a condenser and protected from moisture with a calcium chloride tube was added 12.1 g. (0.1 mole) of benzamide, 2.9 g. (0.05 mole) of potassium fluoride, and 100 ml. of anhydrous benzene. The mixture was refluxed for 25 hr., cooled, and filtered. The solid was washed with cold water and dried to give a recovery of 12.0 g. (99.2%) of benzamide.

N-Methylbenzamide.-- This compound was prepared in 40% yield following the procedure of Brady and Dunn,[21] m.p. 81-82° (lit.[21] m.p. 80-82°).

N-Chloro-N-methylbenzamide (IV).—The method of Burstall, *et al.*,[22] was followed to yield 98% of the product.

Attempted Reaction of N-Chloro-N-methylbenzamide. A. With Potassium Fluoride.—Into a 200-ml., one-necked flask equipped with a condenser and a calcium chloride drying tube was added 2.6 g. (0.016 mole) of N-chloro-N-methylbenzamide, 1 g. (0.017 mole) of potassium fluoride, and 75 ml. of dry benzene. The mixture was refluxed for 15 hr., cooled, and filtered to yield 1.0 g. (100%) of potassium fluoride. The benzene solution was evaporated to yield 2.5 g. (96.1%) of an oil identified as starting material by comparison of its infrared spectrum with an authentic sample.

B. With Cesium Fluoride.—The same procedure as above was followed. Recovery of 2.4 g. (97.2%) of the amide and 2.4 g. (100%) of the fluoride resulted.

N-Chloro-N-benzoyl-N′-phenylurea (V).—The reaction between N-chlorobenzamide and phenyl isocyanate was run in the indicated manner under nitrogen under anhydrous conditions. The reaction mixture was filtered to yield a solid, m.p. 182-189° dec.

Analysis was accomplished by warming 0.9974 g. (0.00364 mole) of the solid in 50 ml. of a 1 *N* NaOH solution and filtering. Filtration afforded 0.8736 g. (0.00364 mole) of N-benzoyl-N′-phenylurea, m.p. 207-208°. The filtrate was diluted to exactly 100 ml. and a 25-ml. aliquot was acidified in the presence of potassium iodide. The liberated iodine was titrated with an 0.1000 *N* sodium thiosulfate solution with starch as an indicator.

Anal. Calcd. for $C_{14}H_{11}ClN_2O_2$: Cl, 12.91. Found: Cl, 12.22.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for the support of this work.

---

[10] Further support for the formation of an anion as an intermediate is the fact that N-bromoacetamide, prepared by the method of E. P. Oliveto and C. Gerold [*Org. Syn.*, **31**, 17 (1951)], did not undergo the Hofmann reaction when treated with potassium fluoride. This can be rationalized by taking into account the stabilizing effect of the benzoyl group in I on the corresponding anion and the destabilizing effect of the methyl group in N-bromoacetamide. This is equivalent to stating that the N-H bond in I is more acidic than the one in the aliphatic amide enhancing the formation of the anion in the former.

[11] J. H. Sanders and R. J. Slocombe, *Chem. Rev.*, **43**, 203 (1948).

[12] R. G. Arnold, J. A. Nelson, and J. J. Verbane, *ibid.*, **57**, 47 (1957).

[13] W. Frankel, M. Hornik, and Y. Levin, *J. Am. Chem. Soc.*, **74**, 3872 (1952). It is noted that N-chlorourethane decomposes violently in ethanol.

[14] J. Stieglitz and R. B. Earle, *Am. Chem. J.*, **30**, 412 (1903).

[15] E. de B. Barnett and C. L. Wilson, "Inorganic Chemistry," Longmans, Green and Co., London, 1958, p. 535.

[16] W. Wagner, "Introduction to Quantitative Analysis," University of Detroit Press, Detroit, Mich., 1959, p. 96.

[17] G. R. Elliot, *J. Chem. Soc.*, **121**, 203 (1922).

[18] R. L. Datta and T. Ghosh, *J. Am. Chem. Soc.*, **35**, 1044 (1913).

[19] M. A. Spielman and F. L. Austin, *ibid.*, **59**, 2658 (1937).

[20] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analyses," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 560.

[21] O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, 2414 (1926).

[22] M. L. Burstall, M. S. Gibson, J. S. Grieg, B. McGhee, and D. G. Stewart, *ibid.*, 3717 (1960).