Communications TO THE EDITOR

The Reaction of *N*-Chlorobenzamide with Potassium Fluoride

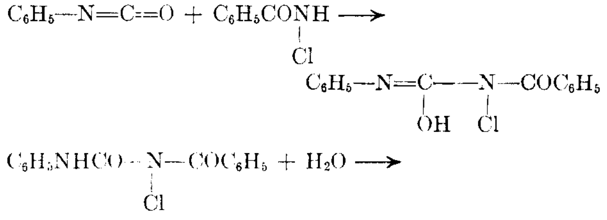
Sir:

We should like to report an unusual example of the Hofmann reaction occurring in a nonaqueous medium. A mixture of 15.5 g. (0.1 mole) of *N*-chlorobenzamide(1) and 2.9 g. (0.05 mole) of anhydrous potassium fluoride in 100 ml. of dry benzene was refluxed for 12 hr., during which time the mixture became orange colored. After cooling, filtration gave 13.5 g. of colorless solid from which the organic material was extracted with and recrystallized from ethanol to yield *N*-benzoyl-*N'*-phenylurea, m.p. 206–208° (reported, 206°).(2) A portion of the alcohol solution gave a positive test for chloride ion with silver nitrate, whereas *N*-chlorobenzamide does not.

This reaction of *N*-chlorobenzamide with potassium fluoride also takes place when dry cyclohexene is used as solvent. Refluxing 15.5 g. (0.1 mole) of *N*-chlorobenzamide with 5.8 g. (0.1 mole) of potassium fluoride gave 14.5 g. of precipitate from which the urea was extracted. This would seem to indicate that formation of phenyl isocyanate is the rate-determining step in the reaction, and is followed by immediate reaction with *N*-chlorobenzamide to form the urea. If this were not the case, the predominant reaction would be simply the formation of a mole of phenyl isocyanate when equimolar proportions of reactants were used. The reaction does not occur in the absence of potassium fluoride, since refluxing a mixture of *N*-chlorobenzamide and dry benzene yields no urea.

A probable mechanism of formation is suggested below, with phenyl isocyanate as the likely intermediate. The same product, *N*-benzoyl-*N'*-phenylurea, was obtained by the authors by refluxing *N*-chlorobenzamide with phenyl isocyanate in dry benzene and purifying the product by recrystallization from ethanol.

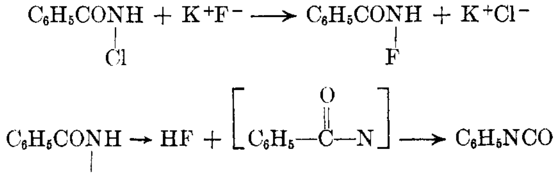
The reaction of *N*-chlorobenzamide with phenyl isocyanate is probably best represented as:



$$C_6H_5{-}N{=}C{=}O + C_6H_5CO\underset{\displaystyle Cl}{\underset{|}{N}}H \longrightarrow C_6H_5{-}N{=}\underset{\displaystyle OH}{\underset{|}{C}}{-}{-}\underset{\displaystyle Cl}{\underset{|}{N}}{-}COC_6H_5$$

$$C_6H_5NHCO{-}\underset{\displaystyle Cl}{\underset{|}{N}}{-}COC_6H_5 + H_2O \longrightarrow C_6H_5NHCONHCOC_6H_5 + HOCl$$

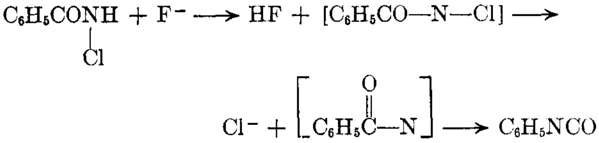
Although the chlorine-containing addition product has not been isolated and identified, it would be anticipated that its hydrolysis would be rapid to yield the urea. Preliminary results do not distinguish between formation of *N*-fluorobenzamide followed by dehydrofluorination and rearrangement,



$$C_6H_5CO\underset{\displaystyle Cl}{\underset{|}{N}}H + K^+F^- \longrightarrow C_6H_5CO\underset{\displaystyle F}{\underset{|}{N}}H + K^+Cl^-$$

$$C_6H_5CO\underset{\displaystyle F}{\underset{|}{N}}H \rightarrow HF + \left[C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}N\right] \longrightarrow C_6H_5NCO$$

and a mechanism involving behavior of fluoride ion as a base:



$$C_6H_5CO\underset{\displaystyle Cl}{\underset{|}{N}}H + F^- \longrightarrow HF + [C_6H_5CO{-}N{-}Cl] \longrightarrow Cl^- + \left[C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}{-}N\right] \longrightarrow C_6H_5NCO$$

The latter would agree with a publication(3) indicating the applicability of fluoride ion as a base for decarboxylation, and with the mechanism of the Hofmann rearrangement in aqueous media. This suggests a possible general usefulness of potassium fluoride as a base in anhydrous media for many reactions, which is currently being studied.

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(1) G. R. Eliot, *J. Chem. Soc.*, **121**, 203 (1922).

(2) M. A. Spielman and F. L. Austin, *J. Am. Chem. Soc.*, **59**, 2658 (1937).

(3) A. N. Nesmeyanov, K. A. Pecherskaya, and G. Y. Uretskaya, *Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk, Izvestiya*, 240 (1948).

Crystalline Glucomannan from Slash Pine

Sir:

In 1951, Yundt(1) reported the isolation of a crystalline fragment from slash pine hemicellulose which contained mannose units. Other sugar units were not fully identified. Later a similar crystalline material was isolated by Nelson(2) who found that glucose as well as mannose residues were present.

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(1) A. P. Yundt, *Tappi*, **34**, 94 (1951).

(2) R. Nelson, Buckeye Cellulose Corp., personal communication.