Communications TO THE EDITOR

The Reaction of *N*-Chlorobenzamide with Potassium Fluoride

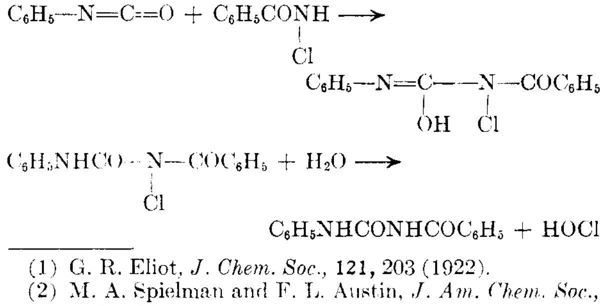
Sir:

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.

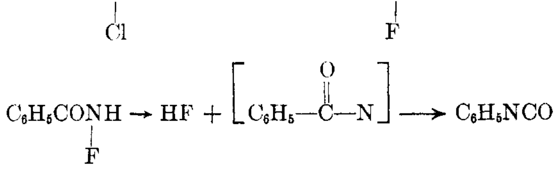
The reaction of *N*-chlorobenzamide with phenyl isocyanate is probably best represented as:



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

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

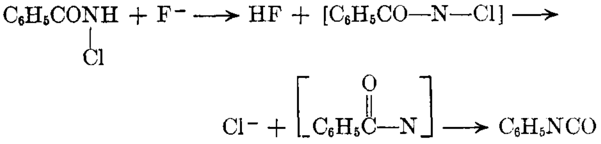
Although the chlorine-containing addition product has not been isolated and identified, it would be anticipated that its hydrolysis would be rapid to yield the urea. Preliminary results do not distinguish between formation of *N*-fluorobenzamide followed by dehydrofluorination and rearrangement,



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

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

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



$$C_6H_5CO\underset{\text{Cl}}{\text{N}}H + F^- \longrightarrow HF + [C_6H_5CO{-}N{-}Cl] \longrightarrow$$

$$Cl^- + \left[C_6H_5\overset{\overset{\text{O}}{\|}}{C}{-}N\right] \longrightarrow C_6H_5NCO$$

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.

Using the techniques suggested by Yundt, with slight modifications, and starting with a slash pine holocellulose, a crystalline glucomannan was isolated, which, on hydrolysis, gave 77% mannose and 23% glucose. Small amounts of ash, but no other sugar units were present.

The sugars were identified chromatographically and by the preparation of crystalline derivatives. The rod-shaped crystals were about 2.5 μ long and showed strong birefringence under polarized light. X-ray powder diagrams and chromatographic data were obtained at various stages of the purification, in the course of which other sugar units (xylose and galactose) were gradually removed. The final X-ray diffraction of the dry material showed relatively sharp peaks.

In future work, the degree of polymerization of the glucomannan fragment, its physicochemical properties, and the oligosaccharides obtained on graded hydrolysis will be studied.

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Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene, 1,2,3,4,5,5-Hexamethylcyclopentadiene, and 1,2,3,4,5-Pentamethylcyclopentadienylcarbinol

Sir:

The author wishes to report the synthesis of the novel compounds: 1,2,3,4,5-pentamethylcyclopentadiene (I), 1,2,3,4,5,5-hexamethylcyclopentadiene (II), and 1,2,3,4,5-pentamethylcyclopentadienylcarbinol (III). These compounds have been unavailable thus far due to inherent difficulties in the exhaustive methylation of cyclopentadiene. They are of obvious interest as nondimerizing cyclopentadiene derivatives, for instance, in photoisomerization reactions.[1] Of special interest are the derived nonclassical cations, one of which is intensely colored.[2]

Preparation of I: Treatment of tiglaldehyde with 2-butenyl-2-lithium[3] gave di(*sec*)-2-butenylcarbinol (IV), b.p. 56.3° (1.5 mm.) n_D^{20} 1.4719 ν(C=C) 1632 cm.$^{-1}$ (m). Oxidation of IV with active manganese dioxide[4] in pentane gave di(*sec*)-2-butenyl ketone (V) in good yield, b.p. 58.0° (4.2 mm.) n_D^{20} 1.4731. $\lambda_{\max}^{C_2H_5OH}$ 239.6, 328 mμ, $\epsilon_{\max}$ 1.22 $\times$ 10^4, 47. ν(C=C—C=O), 1642 cm.$^{-1}$ (vs). Cyclization of V in formic acid–phosphoric acid in accordance with the Nazarov ring closure[5] gave in good yield 2,3,4,5-tetramethylcyclopent-2-en-1-one (VI) b.p. 59.8° (3.3 mm.) n_D^{20} 1.4772. $\lambda_{\max}^{C_2H_5OH}$ 236, 302 mμ; $\epsilon_{\max}$, 1.39 $\times$ 10^4, 97.6. ν(C=O), 1700 cm.$^{-1}$ (vs); ν(C=C), 1650 cm.$^{-1}$ (s). Treatment of VI with methyllithium gave the expected tertiary alcohol as the initial product. Water was lost spontaneously upon addition of a trace of iodine; distillation of the product yielded I (75%), b.p. 58.3° (13.5 mm.) n_D^{20} 1.4748. Mass spec. mol. wt. 136. $\lambda_{\max}^{\text{isooctane}}$ 232 (sh), 248, 265 (sh) mμ $\epsilon_{\max}$ 2780, 3180, 2730. ν(C=C—C=C), 1653 cm.$^{-1}$ (m), 1620 cm.$^{-1}$ (w).

Preparation of II: Addition of I to one equivalent of sodamide[6] in liquid ammonia gave smoothly pentamethylcyclopentadienyl sodium (VII); addition of one equivalent of methyl iodide to VII gave II (67% yield), b.p. 52.8° (6.4 mm.) n_D^{20} 1.4719; mass spec. mol. wt. 150. $\lambda_{\max}^{\text{isooctane}}$ 252.4 mμ $\epsilon_{\max}$ 4140. ν(C=C—C=C) 1654 cm.$^{-1}$ (m), 1620 cm.$^{-1}$ (w). A characteristic strong band occurred at 1080 cm.$^{-1}$ nmr spectrum (40 M.c.) in c.p.s. rel. to internal $Si(CH_3)_4$ capillary: -36.4, rel. area 6 (*gem*-dimethyl); -67.8, rel. area 12 (four vinyl methyl groups).

Preparation of III: VII was prepared as above. The ammonia was removed, finally *in vacuo*. The residue was dispersed in tetrahydrofuran (distilled from lithium aluminum hydride); 1 equivalent of ethyl chloroformate (VIII) was now added. After 1-hr. reflux, sodium chloride was removed by filtration. Tetrahydrofuran and excess VIII were removed by distillation. The ester residue was reduced with lithium aluminum hydride in ether. The product was III in 52% yield, b.p. 65.5° (1.1 mm.) n_D^{20} 1.4955. The distillate crystallized, m.p. 30.5°: λ isoöctane 262.4 mμ (ϵ, 3230); ν(O—H), 3580 cm.$^{-1}$ (vs); ν(C=C—C=C) 1656 cm.$^{-1}$ (m); ν(C—O) 1040 cm.$^{-1}$ (vs).

Anal. Calcd. for I ($C_{10}H_{16}$): C, 88.14; H, 11.86. Found: C, 87.89; H, 12.02. Calcd. for II ($C_{11}H_{18}$): C, 87.90; H, 12.10. Found: C, 87.74; H, 11.91. Calcd. for III ($C_{11}H_{18}O$): C, 79.44; H, 10.93. Found: C, 79.71; H, 10.99. I, II, and III were homogeneous in vapor phase chromatography. Absorption above 3000 cm.$^{-1}$ or at 870–900 cm.$^{-1}$ characteristic of exocyclic methylene is absent in the infrared spectra of all three compounds. IV, V, and VI gave satisfactory C—H analyses.

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(2) L. deVries, *J. Am. Chem. Soc.*, in press.

(3) A. S. Dreiding and R. F. Pratt, *J. Am. Chem. Soc.*, **76**, 1902 (1954).

(4) F. Attenburrow *et al.*, *J. Chem. Soc.*, 1097 (1952).

(5) E. A. Braude and F. A. Coles, *J. Chem. Soc.*, 1430 (1952).

(6) C.R.Hauser *et al.*, *Org. Syntheses*, Coll. Vol. III, 291 (1955).