The reaction of ethoxymethyl acetate with aluminum isopropoxide gave no isolable aluminate of the hemiacetal, but gave acetone, esters which were typical products of Tischtschenko reactions, and a mixture of methyl, ethyl, and isopropyl aluminates.

LEXINGTON, KY. RECEIVED SEPTEMBER 8, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

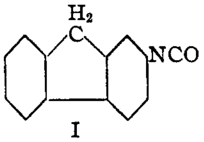
Fluorene Compounds. Nitrogen Derivatives

BY FRANCIS EARL RAY AND GEORGE RIEVESCHL, JR.

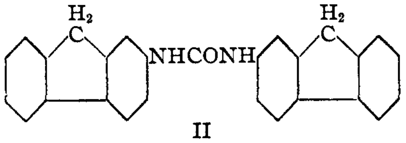
In the present work we undertook the preparation of new derivatives of 2-aminofluorene and of 9-N substituted 2-benzoylfluorene.

The preparation of 2-aminofluorene was first accomplished by Strasburger[1] from 4-aminodiphenic acid. A more convenient synthesis by the reduction of the normal mono-nitration product of fluorene is described in "Organic Syntheses."[2]

When we attempted to prepare 2-fluoryl-isocyanate, I, from the amine and phosgene, the *sym*-di-urea resulted, II.



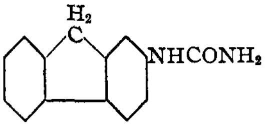
I



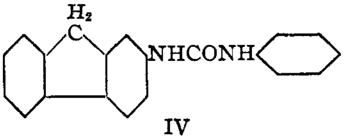
II

The isocyanate, I, was obtained by the modification of Hardy.[3] When dry it was quite stable but moisture caused its conversion into the di-urea, II. This di-urea was formed quantitatively when equimolar solutions of 2-aminofluorene and 2-fluoryl isocyanate were mixed.

When treated with ammonia, the mono-urea, III, was obtained. *sym*-Phenyl-2-fluorylurea, IV, was prepared in two ways: by treating 2-fluoryl isocyanate with aniline and by treating 2-aminofluorene with phenyl isocyanate.



III



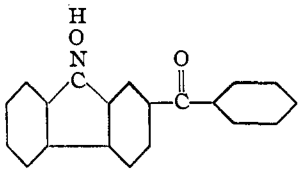
IV

Due to the sensitivity of 2-fluoryl isocyanate to water and the insolubility of the resulting di-urea in ether, acetone, etc., it may be a useful reagent to detect small amounts of water. The factor is 0.0464.

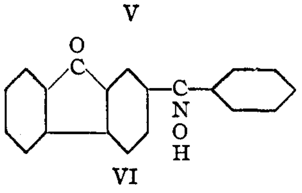
The methyl, ethyl and *n*-propyl urethans were prepared from 2-fluoryl isocyanate and the corresponding absolute alcohol.

Derivatives of 2-Benzoylfluorene

In 1902 Fortner[4] prepared a monoxime from 2-benzoylfluorenone which he described as bright yellow leaves from alcohol which sintered at 185° and melted at 199°. Fortner did not determine which of the configurations, V or VI, this compound possessed.



V



VI

As it seemed probable that the 9-position of the fluorene would be the more active, we set out to prepare V by methods that would leave no doubt as to its constitution.

Using Nenitzescu and Isăcescu's[5] method we condensed benzyl chloride with potassium 2-benzoyl-9-*aci*-nitrofluorene[6] and obtained an oxime melting at 207–208°.

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[1] Strasburger, *Ber.*, **16**, 2346 (1883).

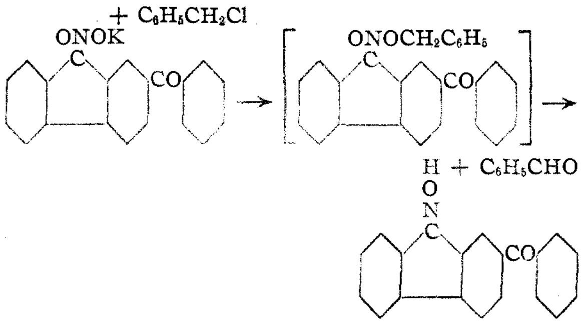
[2] *Org. Syntheses*, **13**, 74 (1933).

[3] Hardy, *J. Chem. Soc.*, 2011 (1934).

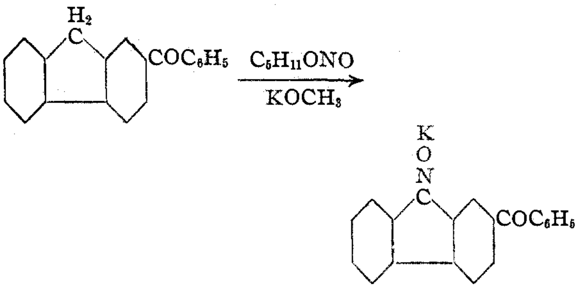
[4] Fortner, *Monatsh.*, **23**, 921 (1902).

[5] Nenitzescu and Isăcescu, *Ber.*, **63**, 2484 (1930).

[6] Ray and Palinchak, in press.



As this was somewhat troublesome to purify we also carried out the preparation by the method of Wislicenus and Waldmüller.[7]



In carrying out this reaction in an ether–benzene mixture some material seemed to precipitate out after standing several hours. On evaporating the filtrate to small volume and adding ether, a second batch of crystals was obtained.

Each was separately acidified and recrystallized. The first (insoluble), α, melted at 213–214° and was a pale yellow powder. The second, β, was obtained in long, golden needles melting at 207–208°.

As neither of these corresponded to the description of Fortner's compound we prepared some material by his directions. It is true that this material first melted at 198–199° but on repeated crystallization, first from benzene and then from alcohol, we obtained the compound in long needles melting at 207–208°, identical with our lower melting, β, oxime. We then mixed equal portions of our two oximes and on recrystallization the mixture melted at about 199°.

To characterize further these oximes the acetyl derivatives were prepared. That from the α-oxime (213–214°) melted at 144–145° while the acetyl derivative of the β-oxime (207–208°) melted at 150–151°. A mixed melting point mixture sintered at 116–126°. Which of these is *cis* and which *trans* remains to be determined.

Moore and Huntress[8] reported the melting point of *syn*-2-nitrofluorenone oxime, prepared in an alkaline solution, as 262.5–263°. Langecker,[9] preparing the oxime in a neutral solution, reported the melting point to be 249°. With this possible exception no other fluorenone oxime has been isolated in *cis* and *trans* forms.

Experimental

2-Aminofluorene was prepared by the method described in "Organic Syntheses."[2] It melted at 127°.

2-Fluoryl Isocyanate.—Eleven grams of 2-aminofluorene was dissolved in 250 cc. of warm toluene and dry hydrogen chloride was passed in until saturation was reached. The 2-aminofluorene hydrochloride separated as a cream-colored mass. The flask was heated to gentle reflux and a steady stream of carbonyl chloride was passed into the mixture. The precipitate gradually dissolved until at the end of one and one-half hours a clear liquid was obtained.

The solution was filtered and the toluene removed under diminished pressure. The tan colored product was recrystallized from ligroin. A pure white product was obtained melting at 69–70° which was readily soluble in most organic solvents. The yield was 11.2 g. or 89%.

Anal. Calcd. for $C_{14}H_9ON$: N, 6.76. Found: N, 6.85.

Methyl 2-fluorylcarbamate was prepared in the usual manner. It crystallized in shining laminae and melted at 118°.

Anal. Calcd. for $C_{15}H_{13}O_2N$: N, 5.85. Found: N, 5.92.

Ethyl 2-fluorylcarbamate was obtained as white plates from ligroin; m. p. 121–122°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: N, 5.53. Found: N, 5.75.

n-**Propyl 2-fluorylcarbamate** also crystallized in plates; m. p. 113°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: N, 5.24. Found: N, 5.58.

2-Fluorylurea was prepared by passing dry ammonia gas into an ether solution of 2-fluoryl isocyanate. It was obtained as plates from alcohol. It did not melt at 360°.

Anal. Calcd. for $C_{14}H_{12}ON_2$: N, 12.49. Found: N, 12.67.

sym-Phenyl-2-fluorylurea was prepared from aniline and 2-fluoryl isocyanate and also by the reaction between 2-aminofluorene and phenyl isocyanate. White cottony fibers were obtained from dioxane, melting at 305° (block).

Anal. Calcd. for $C_{20}H_{16}ON_2$: N, 9.33. Found: N, 9.37.

sym-Di-2-fluorylurea was prepared from the isocyanate and 2-aminofluorene and also by treating the isocyanate with water. White cottony clusters were obtained from pyridine which did not melt at 360°. It is insoluble in most organic solvents.

Anal. Calcd. for $C_{27}H_{20}ON_2$: N, 7.21. Found: N, 7.37.

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(7) Wislicenus and Waldmüller, *Ber.*, **41**, 3334 (1908).

(8) Moore and Huntress, THIS JOURNAL, **49**, 1324, 2618 (1927).

(9) Langecker, *J. prakt. Chem.*, **132**, 145 (1931).

2-Benzoylfluorene was prepared by Perrier's[10] modification of the Friedel–Crafts reaction. It melted at 122°.

Potassium 2-benzoyl-9-aci-nitrofluorene was obtained by the method of Ray and Palinchak.[6]

2-Benzoyl-9-fluorenoneoxime.—Three and one-half grams of potassium 2-benzoyl-9-*aci*-nitrofluorene, 3.5 g. of benzyl chloride and 40 cc. of 95% alcohol were refluxed for eight hours. Potassium chloride slowly separated and the orange color faded to yellow. The solution was filtered and treated with water. An oil separated which solidified on stirring. After three recrystallizations from alcohol the melting point was 207–208° (β-form).

As this material was somewhat difficult to purify we condensed 27 g. of 2-benzoylfluorene with 13.7 cc. of isoamyl nitrite in the presence of 5.5 g. of potassium in 30 cc. of absolute methyl alcohol, 100 cc. of anhydrous ether and 200 cc. of pure benzene.

The product that precipitated weighed 16.1 g. It was separated, acidified and recrystallized from alcohol. This α-form of the oxime was obtained as a pale yellow powder melting at 213–214°.

Anal. Calcd. for $C_{20}H_{13}O_2N$: N, 4.67. Found: N, 4.66.

The acetyl derivative was prepared with acetyl chloride in pyridine–ether solution. Greenish-yellow fibers were obtained that melted at 144–145°.

Anal. Calcd. for $C_{22}H_{15}O_3N$: N, 4.11. Found: N, 4.31.

β-Oxime.—The filtrate from the α-potassium salt was evaporated to 50 cc. and 500 cc. of ether was added. The precipitate weighing 12.4 g. was separated, acidified and recrystallized three times from alcohol. Long, bright yellow crystals were obtained melting at 207–208°. These were identical with those prepared by Fortner's[4] method.

Anal. Calcd. for $C_{20}H_{13}O_2N$: N, 4.67. Found: N, 4.63.

This acetyl derivative crystallized in brilliant yellow plates that melted at 150–151°.

Anal. Calcd. for $C_{22}H_{15}O_3N$: N, 4.11. Found: N, 4.33.

Summary

The following new compounds of fluorene have been prepared: 2-fluoryl isocyanate; methyl, ethyl and *n*-propyl 2-fluorylcarbamate; 2-fluorylurea; *sym*-phenyl-2-fluorylurea; *sym*-di-2-fluorylurea; and the potassium salts and the acetyl derivatives of the α- and β-9-oximes of 2-benzoylfluorenone, as well as the free α- and β-oximes.

The compound obtained by the reaction between 2-benzoylfluorenone and hydroxyl amine reported by Fortner[4] is shown to have been a mixture of the α- and β-forms of the 9-oxime.

CINCINNATI, OHIO RECEIVED SEPTEMBER 2, 1938

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[10] Perrier, *Bull. soc. chim.*, [3] **31**, 859 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Analytical Separation of Various Classes of Sugars

BY CHARLES D. HURD AND SIDNEY M. CANTOR[1]

The purpose of this investigation was to develop a method for the separation of various classes of sugars, such as monosaccharoses from di- or trisaccharoses, or pentoses from hexoses. It was hoped that the method would achieve not only separation but also analysis of the mixture as well. The importance of a direct method of analysis is obvious, in view of the fact that most of the analytical methods which have been suggested for sugars are empirical and depend largely on a preëxisting knowledge of the identity of the sugar. Methods based on the reducing action of copper salts or on the preferential fermentation by specific microörganisms are obviously limited in scope.

Methylation and fractional distillation of sugar mixtures appeared to be the most promising plan of attack for several reasons: (1) the methyl ethers are known to distil *in vacuo* without decomposition, (2) sizable boiling point differences exist between the methyl ethers of the sugar classes, (3) the methylation procedure would be satisfactory on a wide variety of sugars since it brings about no serious structural changes, (4) the fact that physical constants of a large number of methylated sugars are known would be of help in subsequent identifications.

Preliminary experiments indicated the feasibility of the plan but they also demonstrated the inapplicability of the customary procedure of direct methylation of the sugar by Haworth's method. For example, glucose, lactose and sucrose were methylated by means of methyl sulfate and alkali and the methylated derivatives distilled. The yields, respectively, were 50, 45 and 46%. These results seemed acceptable but it was found that no such uniformity in yields was at-

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[1] Corn Products Refining Company Fellow, 1933–1936.