TABLE I

HYDROGENATION OF β-ANILINOCROTONOPHENONE (C) AND THE ETHYL ESTERS OF SUBSTITUTED METHYLENEMALONIC (M) AND ACETOACETIC ACIDS (A)

Run	Compound	Cat.	Moles H_2	P., atm.	T, °C.	Time min.	% Products isolated
1	C_6H_5NH-M	PtO_2	1	2	25	50	35 Aniline; 3.6 diphenylurea
2	NH_2-M	PtO_2	0.25	2	25	60	Ammonia
3	$C_6H_5N(CH_3)$-M	PtO_2	2	2	25	394	55 Methylaniline, 55 diethyl methylmalonate
4	Same	Ni(R)	2	60	67	112	67 Methylaniline, 72 diethyl methylmalonate
5	C_6H_5NH-A	PtO_2	2.5	1	25	282	[a]
6	Same	PtO_2	2	2	25	270	32 Aniline, 24 ethyl methylacetoacetate
7	NH_2CONH-A	PtO_2	1.67	2	25	214	43 Ethyl 2-ureidomethyl-3-hydroxybutanoate, 24 ethyl methylacetoacetate
8	C_6H_5CONH-A	Ni(R)	1.75	60	68	145	30 Ethyl benzamidomethylacetoacetate[b]
9	CH_3CONH-A	Ni(R)	1.1	60	67	37	0 Acetamide
10	C	Ni(R)	1.67	60	68	150	79 Aniline, 40 butyrophenone
11	C[c]	PtO_2	2	2	27	30	79 Aniline, 91 butyrophenone

[a] This was a micro run for maximum hydrogen uptake. [b] Yield based upon dinitrophenylhydrazone obtained. [c] Absolute ethyl acetate was used as solvent.

ether to the hot solution. The white crystals, m. p. 103°, weighed 5 g. The ferric chloride test is negative and haloform test is positive.

Anal. Calcd. for $C_8H_{16}N_2O_4$: N, 13.61. Found: N, 13.37.

Ethyl Benzamidomethylacetoacetate.—It was not practical to isolate this compound from the reaction mixture (Run No. 8). When the mixture was subjected to distillation at 170–200° at 4 mm. there was obtained by precipitation with ether crude benzamide, m. p. 117° and mixed m. p. 122°, and an ether soluble oil, probably methyleneacetoacetic ester which slowly polymerized to a semi-solid gel. That these products were formed by pyrolytic decomposition of the benzamidomethylacetoacetic ester was proved by preparing from the unheated reaction product its *2,4-dinitrophenylhydrazone*, yellow plates, m. p. 157–157.5°, from alcohol.

Anal. Calcd. for $C_{20}H_{21}N_5O_7$: C, 54.17; H, 4.75; N, 15.80. Found: C, 54.09; H, 4.89; N, 15.69.

Butyrophenone was isolated from the ether-soluble neutral fractions from Runs No. 10 and 11 by distillation *in vacuo*, and was converted into its 2,4-dinitrophenylhydrazone, m. p. 186–187°; lit.[13] 190°.

Summary

1. Open chain vinylogs of the amides are as easily cleaved by hydrogenation as are the ester vinylogs.

2. The vinylogs of N-acylamides are more resistant to cleavage and may be hydrogenated at the olefinic linkage.

3. The formation of a derivative from ethoxymethylenemalonic ester and methylaniline and the similarity of its behavior on hydrogenation to the derivatives of primary amines indicates that these latter compounds are substituted acrylic esters and not anils.

(13) Evans, *J. Chem. Soc.*, 785 (1936).

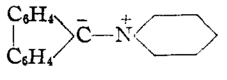
EVANSTON, ILLINOIS RECEIVED JUNE 10, 1946

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, SOILS AND AGRICULTURAL ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Behavior of Certain Fluorene Compounds Containing Trivalent Carbon and Tetravalent Nitrogen

BY LOUIS A. PINCK AND GUIDO E. HILBERT[1]

This paper deals with the behavior of three interesting compounds, which have a trivalent carbon and a tetravalent nitrogen, namely, fluorylidenepyridinium I, fluorylidene-α-picolinium II and fluorylidene-9-ammonium fluorene III. Compounds of this type, namely, fluorylidene trimethylammonium and fluorylidene triethylammonium, had been reported by Ingold and Jessop.[2] Their attempts to isolate them met with failure because of the instability of these compounds. In an article by Krollpfeiffer and Schneider,[3] it was briefly mentioned that deep blue colored products (presumably fluorylidene pyridinium) could be prepared from 9-fluorylpyridinium bromide. The preparation of the sulfur analog, namely, fluorylidene dimethyl sulfide had been reported by Ingold and Jessop,[4]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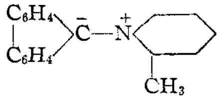
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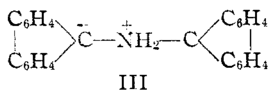
III

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[1] Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.

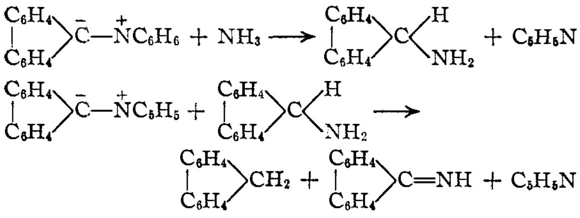
(2) Ingold and Jessop, *J. Chem. Soc.*, 2357 (1929).

(3) Krollpfeiffer and Schneider, *Ann.*, **530**, 38 (1937).

(4) Ingold and Jessop, *J. Chem. Soc.*, 713 (1930).

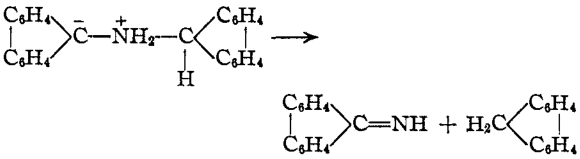
and we had found that this compound rearranges to fluorene-1-dimethyl sulfide.[5] A similar rearrangement of the nitrogen analog was reported by Sommelet,[6] who found that benzohydryltrimethylammonium hydroxide under thermal or photochemical action yielded in addition to other products N-dimethyl-*o*-benzylbenzylamine.

The hydrobromide salts of I and II were obtained by solvolysis of 9-bromofluorene in pyridine and α-picoline, respectively. Compounds I and II were prepared by treating the salts with aqueous and alcoholic solutions of alkali and with liquid ammonia. As a result of this treatment indigo blue solutions and dark colored solids were formed and the free bases were found to be too unstable for isolation. Due to their instability solutions of I and II contained in sealed tubes appeared to remain unaltered only for several days. Upon longer standing the indigo blue color changed to a bluish green, and from the reaction mixture fluorene and fluorylidene-imine were isolated. The decomposition may be presented by the following reactions



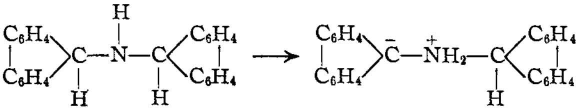
9-Aminofluorene which is initially formed is consumed in the second reaction. This type of dehydrogenation of 9-aminofluorene had been demonstrated with certain unsaturated compounds which are much more stable than those presented in this study.[7] In an aqueous medium 9-fluorenol would be the intermediate, and fluorenone one of the end-products.

The third compound for which we have assigned structure III is similar in its physical and chemical properties to I and II. Like the others it has a great avidity for oxygen of the atmosphere, imparts an indigo blue color to its solvent and yields similar products when decomposed in ammonia as indicated in the reaction

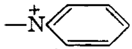


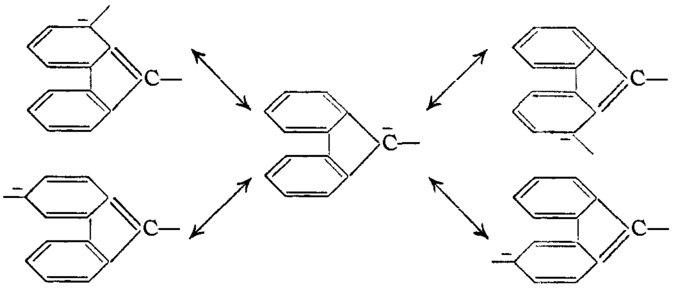
When III is decomposed in alcoholic sodium hydroxide the reaction mixture yields 9-aminofluorene and, in addition to the products indicated above, a compound the analysis of which corresponds to an ethylaminofluorene. Although III is much more stable than either I or II, various attempts to isolate it yielded negative results.

Fluorylidene-9-ammonium fluorene III was obtained by rearrangement of 9,9′-difluorylamine in alkali or in liquid ammonia, which involved a shift of a hydrogen from carbon to nitrogen. 9,9′-Difluorylamine[8] was prepared by the interaction of



9-bromofluorene with 9-aminofluorene in acetonitrile.

Although compounds I, II and III cannot be considered dyes, the resonance phenomenon of dyes is applicable to them. Bury[9] stated that the intense absorption of light characterizing dyes is due to an intimate association of a chromophore and of resonance in a molecule and that the function of the auxochrome is to introduce the possibility of resonance. The auxochrome is a group having such elements that can readily change their covalence by one unit and are limited to nitrogen, oxygen and occasionally sulfur.[10] From the standpoint of resonance the distinguishing differences between the compounds presented in this communication and dyes are that these compounds possess a fixed tetravalent nitrogen as in  and , and that the carbon has a shifting covalence as shown below



Here the carbon may be considered as the auxochromic element.

Acknowledgment.—We wish to express our appreciation to Mrs. M. S. Sherman for carrying out the recorded microanalyses.

Experimental

9-Fluorylpyridinium hydrobromide was obtained by letting a solution of 30 g. of 9-bromofluorene in 100 cc. of anhydrous pyridine stand at room temperature for several weeks. The precipitate that was formed was removed and washed with hexane until free from pyridine; yield 35 g. (88.4%). It was crystallized from 35 cc. of alcohol yield-

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[5] Hilbert and Pinck, THIS JOURNAL, **60**, 494 (1938); Pinck and Hilbert, *ibid.*, **68**, 751 (1946).

[6] Sommelet, *Compt. rend.*, **205**, 56 (1937).

[7] Pinck and Hilbert, THIS JOURNAL, **54**, 710 (1932).

[8] Goldschmidt and Reichel, *Ann.*, **456**, 163 (1927).

[9] Bury, THIS JOURNAL, **57**, 2115 (1935).

[10] Brooker, "Advances in Nuclear Chemistry and Theoretical Organic Chemistry," Interscience Publishers, New York, N. Y., 1945, pp. 63–136.

ing large rhombohedral crystals, m.p. 209° (orange red melt).

Anal. Calcd. for $C_{18}H_{14}NBr$: C, 66.66; H, 4.37; N, 4.32. Found: C, 66.78; H, 4.57; N, 4.38.

An alcoholic solution of the hydrobromide became indigo blue upon the addition of sodium hydroxide. After several hours the color of the solution changed to green then orange and finally red. When an aqueous solution of the hydrobromide was treated with alkali a deep purplish blue precipitate was deposited which was found to be soluble in most organic solvents and decomposed within an hour. Another specimen was treated with liquid ammonia in a sealed tube. The indigo blue color of the solution changed on the fifth day to a bluish green. Fluorene and fluorylidene-imine were isolated from the reaction mixture.

9-Fluoryl α-picolinium hydrobromide was prepared by the interaction of 18 g. of 9-bromofluorene with 35 cc. of α-picoline in a sealed tube at 100° for two hours. The brownish red mother liquor was decanted and the precipitate was well washed with hexane, yield 18.3 g. (72.2%). It was twice recrystallized from alcohol, hexagonal prisms, m.p. 197–198° (red melt).

Anal. Calcd. for $C_{19}H_{16}NBr$: C, 67.47; H, 4.77; N, 4.14. Found: C, 67.56; H, 4.77; N, 4.31.

The behavior of II is very similar to that of I.

9,9'-Difluorylamine.—The hydrobromide salt was obtained by the reaction of 4 g. of 9-bromofluorene with 3 g. of 9-aminofluorene in 40 cc. of acetonitrile, yield 5.3 g., m.p. 203° (dec.). The free amine was obtained by boiling an alcoholic solution of the hydrobromide under reflux for several hours and the product thus obtained was crystallized from benzene, needles, m.p. 201° (light green melt).

Anal. Calcd. for $C_{26}H_{19}N$: C, 90.39; H, 5.55; N, 4.06. Found: C, 90.46; H, 5.68; N, 4.11.

Rearrangement of 9,9'-Difluorylamine

In Ammonia.—A solution of 0.25 g. of 9,9'-difluorylamine in 10 cc. of liquid ammonia turned indigo blue within an hour. The dark blue color remained unaltered for over a half a year. However, after standing for three quarters of a year it had changed to a light bluish green. The ammonia was evaporated and the reaction mixture was triturated with ether, which when saturated with hydrogen chloride yielded the orange colored hydrochloride of fluorylidene-imine. The free base and a mixture with fluorylidene-imine melted at 124°. The ether-hydrochloric acid soluble fraction was sublimed yielding fluorene and leaving only a trace of material which was not identified.

In Alcohol.—In a preliminary run 1 g. of difluorylamine hydrobromide in a solution of 30 cc. of ethyl alcohol containing 2 g. of sodium hydroxide was heated at 100° in a sealed tube. It was observed that the solution turned light blue when first heated and that upon shaking the tube the color faded out completely. This phenomenon was repeated several times, and thereafter the color persisted. The salt was quite insoluble and only after about one hour of heating did an appreciable amount dissolve and impart an indigo blue color to the solution.

It was felt that the fading of the color was due to a reaction with the oxygen in the tube, and so the experiment was repeated using 2 g. of the amine salt, 2.5 g. of sodium hydroxide and 30 cc. of alcohol. The tube was evacuated prior to its being sealed and as anticipated the initial blue color did not fade. In this experiment it took five hours of heating at 100° for the blue solution to turn green and six and one-half hours till it changed to yellow. The alcohol was removed and the residue was extracted with benzene. The latter was treated with hydrogen chloride effecting an initial deposition of a colorless hydrochloride and then an orange one, weight 0.65 g. All of the colored and some of the colorless hydrochlorides were extracted with boiling chloroform. The insoluble fraction (0.3 g.) was recrystallized from dilute hydrochloric acid yielding colorless needles, m.p. 250° (dec.), mixed m.p. with 9-aminofluorene hydrochloride unchanged.

Anal. Calcd. for $C_{13}H_{12}NCl$: N, 6.44. Found: N, 6.47.

In an attempt to isolate the fluorylidene-imine hydrochloride from the chloroform extract it was found futile on account of the presence of the colorless hydrochloride. It was therefore hydrolyzed and the resulting fluorenone was converted to the sparingly soluble fluorenone ketazine,[11] weight 0.075 g., m. p. and mixed m. p. with an authentic specimen 269°. The benzene hydrogen chloride soluble fraction consisting of yellow crystals (possibly fluorenone) and a reddish oily substance was subjected to sublimation whereby 0.25 g. of crude fluorene was obtained, which upon recrystallization from hexane melted at 113°, mixed m. p. with fluorene 114°. The unsublimed residue was taken up in benzene and several extractions were made with very dilute hydrochloric acid. By concentration of the extracts 0.13 g. of hydrochloride was obtained, m. p. 276°. This was converted to the free base forming a sirupy resin which failed to crystallize even after standing in a desiccator for five weeks. The base, which presumably is considered to be an ethylamino-fluorene, was again converted to the hydrochloride yielding needle-like prisms, m.p. 276°.

Anal. Calcd. for $C_{15}H_{16}NCl$: C, 73.29; H, 6.57; N, 5.70. Found: C, 73.47; H, 6.72; N, 5.71.

The residual benzene soluble fraction was a brown oily resin which failed to crystallize from various organic solvents.

Summary

The hydrobromides of fluorylidenepyridinium and fluorylidene-α-picolinium were obtained by solvolysis of 9-bromofluorene in pyridine and in α-picoline. In an alkaline medium they formed the free bases yielding indigo blue solutions and dark colored solids. Their stability in solution ranged from a few hours to several days. In liquid ammonia they ammonolyzed forming fluorene, fluorylidene-imine and pyridine or α-picoline.

Fluorylidene-9-ammonium fluorene was obtained by the rearrangement of difluorylamine in an alkaline medium forming an indigo blue colored solution. In liquid ammonia it appeared to be stable for more than a half a year. However, after nine months it was decomposed into fluorene and fluorylidene-imine. In alcoholic sodium hydroxide it yielded in addition to the above-named products, 9-aminofluorene, an ethylaminofluorene and an oily resin which was not identified.

These compounds have a tetravalent nitrogen and a trivalent carbon.

BELTSVILLE, MARYLAND RECEIVED MAY 9, 1946

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[11] Pinck and Hilbert, THIS JOURNAL, 57, 2400 (1935).