After the acid was precipitated by dilution with ice and water, the product was filtered and washed twice with hot water. The product was digested in warm, dilute hydrochloric acid, filtered and washed well with hot water. The insoluble material was digested in 500 cc. of water containing 45 g. of sodium carbonate. The hot solution was treated with norite and filtered. The filtrate was acidified with cold, concentrated hydrochloric acid and the precipitate filtered and dried overnight at 80°. Crystallization from acetic acid gave 55.5 g. of the desired acid, brownish-red needles, m. p. 193.4–195.4°. A sample recrystallized from acetic acid had a melting point of 196.8–197.6°. The alkali insoluble material was treated with aqueous sodium bisulfite,[6] the mixture filtered and the filtrate acidified with concentrated sulfuric acid. The precipitated material was filtered and twice recrystallized from ethanol giving red brown crystals of fluoranthenequinone, m. p. 193.0–193.8°.[7]

Ethyl Fluorenone-1-carboxylate.—The keto acid, I, was esterified with ethanol and hydrogen chloride in the usual way. The ester was isolated as gold-yellow crystals after two crystallizations from ethanol, m. p. 84.8–85.4°; reported melting point, 75–76[8] and 84–86°.[9] On a third recrystallization from ethanol, the crystals had a melting point of 76.0–76.5°. After melting, the melt was cooled and the solid remelted whereupon softening took place at 76° and sharp liquefaction occurred at 84.0–84.8°. Both the high and low melting forms gave identical ultraviolet absorption spectra.

Methyl Fluorenone-1-carboxylate.—This compound was prepared from I with methanol and hydrogen chloride and was crystallized from methanol as yellow needles, m. p. 86.6–87.4°; reported[9] melting point, 86–89°.

Fluorenone-1-carboxamide.—The keto acid, I, was converted *via* the chloride to the amide which was crystallized from acetic acid and separated as yellow-orange crystals, m. p. 235.8–237.0°; reported melting point, 229–230°,[8] and 226.5–227°.[10]

1-Aminofluorenone.—The Hofmann reaction on the amide gave the aminofluorenone. The amine was recrystallized first from ethanol and then from petroleum ether and was thus obtained as orange plates, m. p. 119.0–120.0°; reported melting point, 110°[8] and 118–118.5°.[10]

Fluorene-1-carboxylic Acid, II.—The keto acid, I, was reduced by the Huang-Minlon modification[11] of the Wolff-Kishner reduction. A mixture of 16.6 g. of I, 10 g. of sodium hydroxide, 10 cc. of 85% hydrazine hydrate and 130 cc. of trimethylene glycol was refluxed for three hours. The temperature of the boiling contents was about 150°. The condenser was removed and the boiling continued in the open (hood) until the temperature in the flask was about 205°. At this point refluxing was resumed and continued for two and one-half hours. The mixture was cooled and poured into ice and hydrochloric acid. The precipitate was filtered and dried overnight. Crystallization from acetic acid gave 13.0 g., m. p. 246–249° as a first crop and 1.0 g., m. p. 243–246° (90% yield) as a second crop. The reduction of the keto acid has been done previously[5] with sodium amalgam but in much poorer yield and we are indebted to Dr. Fieser for suggesting the application of the above procedure to improve his yield.

Methyl Fluorene-1-carboxylate, III.—A suspension of 5.16 g. of II in 100 cc. absolute methanol was saturated with hydrogen chloride and the ester isolated in the usual way. Crystallization of the ester from methanol gave 4.94 g. of colorless crystals, m. p. 86.6–87.4°. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 80.4; H, 5.2.

Ethyl fluorene-1-carboxylate was prepared from ethanol and II as above. Crystallization from ethanol gave colorless crystals, m. p. 53.6–54.8°. *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.9; H, 5.8.

Fluorene-1-carboxamide was prepared from II *via* the acid chloride. Crystallization from acetic acid gave colorless crystals, m. p. 251.0–253.0°. *Anal.* Calcd. for $C_{14}H_{11}ON$: C, 80.4; H, 5.3. Found: C, 79.8; H, 5.1.

Hydrazide of Fluorene-1-carboxylic Acid, IV.—A solution of 5.0 g. of the methyl ester, III, 20 cc. of absolute ethanol and 5 cc. of 85% hydrazine hydrate was refluxed for twenty-four hours. A white solid appeared during the refluxing. The mixture was cooled and filtered and washed with ethanol to give 3.84 g. of white fluffy needles, m. p. 216.6–218°. *Anal.* Calcd. for $C_{14}H_{12}N_2O$: N, 13.2. Found: N, 13.0.

1-Fluorenylurethan, V.—A solution of 1.06 g. of IV in 20 cc. of glacial acetic acid was treated with 0.5 cc. of concentrated hydrochloric acid. The suspension was cooled to 0° and 0.8 g. of sodium nitrite in 5 cc. of water added. The suspension was stirred in the cold for one hour then at room temperature for one hour. The mixture was diluted with water and filtered. The precipitate was washed with water and dried in a vacuum desiccator. The solid weighed 1.00 g.; it melted at 85° with gas evolution and was very soluble in organic solvents. *Anal.* Calcd. for $C_{14}H_9N_3O$; N, 17.9. Found: N, 18.6. A solution of 0.85 of the crude azide in 25 cc. of absolute ethanol was warmed to about 70°. Rapid gas evolution occurred. The solution was then refluxed for two hours. The solution was filtered from a small amount of insoluble material and the filtrate concentrated. The urethan (0.62 g.) was obtained from ethanol as colorless plates, m. p. 132.0–132.6°. *Anal.* Calcd. for $C_{16}H_{15}NO_2$: N, 5.6. Found: N, 5.8.

1-Aminofluorene.—A mixture of 0.5 g. of the urethan, V, 10 cc. of acetic acid and 15 cc. of concentrated hydrochloric acid was heated in a sealed tube at 140° for four hours. After cooling, the tube was opened, the contents diluted with water and filtered. The insoluble material (m. p. > 270°) was placed in a separatory funnel with 10% potassium hydroxide solution and ether. After shaking for several minutes, the solid disappeared. The ether layer was separated and evaporated to dryness and the residue crystallized from dilute ethanol to give 0.31 g. of tan crystals, m. p. 117–119°; recrystallized from benzene–petroleum ether, m. p. 124.0–124.6°. *Anal.* Calcd. for $C_{13}H_{11}N$: N, 7.7. Found: N, 8.0. The trinitrofluorenone complex[12] separated from benzene as beautiful, almost black needles, m. p. 211.0–211.8°. *Anal.* Calcd. for $C_{26}H_{16}N_4O_7$: N, 11.3. Found: N, 11.3.

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[6] The procedure described in *Org. Syntheses*, **24**, 1 (1944), for the isolation of acenaphthenequinone was used.

[7] Fittig and Liepmann, *Ann.*, **200**, 5 (1879).

[8] Goldschmeidt, *Monatsh.*, **23**, 894 (1902).

[9] Goldschmeidt and Lipschitz, *ibid.*, **25**, 1175 (1904). In this article the authors state that the melting point of 75–76° reported for the ethyl ester in their earlier work (ref. 8) was a misprint. However, in view of our isolation of a low melting form, it is quite possible that their early observation was genuine. The melting point of our low melting form did not change even after standing more than a year.

[10] Huntress, Pfister and Pfister, THIS JOURNAL, **64**, 2846 (1942).

[11] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[12] Orchin and Woolfolk, *ibid.*, **68**, 1727 (1946); Orchin, Reggel and Woolfolk, *ibid.*, **69**, 1225 (1947).

WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
RECEIVED NOVEMBER 12, 1948

On the Structure of Aromatic Aldehyde Semicarbazones[1]

BY GIUSEPPE CILENTO

By chemical evidence, structure (I) has been attributed to the semicarbazones. The enolic structure (II), although it might explain the abnormal ultraviolet absorption maximum of these compounds, has been ruled out, since essentially

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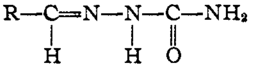
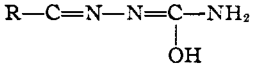
[1] This investigation was supported by a grant from the Fundação Virginia Matarazzo, São Paulo, Brazil.

the same light absorption is shown by the corresponding N-methyl semicarbazones, where enolization cannot occur.[2] Additional information has been obtained by investigating the ultraviolet absorption spectra of aqueous solutions of benzaldehyde and *p*-nitrobenzaldehyde semicarbazones at different hydrogen ion concentrations.



$$R-\underset{H}{\underset{|}{C}}=N-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-NH_2$$

(I)

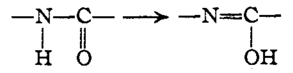


$$R-C=N-N=\underset{OH}{\underset{|}{C}}-NH_2$$

(II)

The spectrum of benzaldehyde semicarbazone remains almost the same in the range from *p*H 2.6 to 11.0, showing $\lambda_{max.}$ = 278 mμ, (Fig. 1). We conclude that the same kind of molecule must be present in these solutions.

That there is one kind only, and that kind must have the carbonyl structure, can be supported by energetic considerations, as the enol formation would be accompanied by an increase of ten kilocalories/mole.[3]



$$-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}- \longrightarrow -N=\underset{OH}{\underset{|}{C}}- \quad \Delta H = +10\text{ kcal./mole}$$

This cannot be overbalanced by the extra resonance energy.

At *p*H 1.0 the spectrum of benzaldehyde semicarbazone is modified, showing a new band at shorter wave length ($\lambda_{max.}$ = 249 mμ). The intensity of the new band increases and that of the original band decreases with time, but after four hours we noticed no further change (Fig. 1).

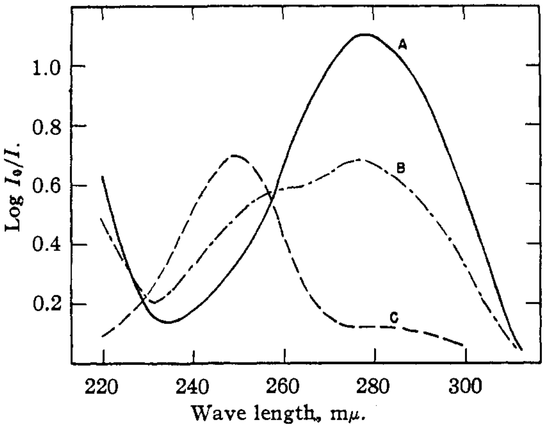


Fig. 1.—Ultraviolet absorption spectrum of benzaldehyde semicarbazone in aqueous solution: A, *p*H 11.0, *p*H 6.0 and *p*H 2.6; B, *p*H 1.0; C, *p*H 1.0 after four hours.

It is very probable that this alteration results from chemical, rather than physico-chemical changes. However, the possibility of hydrolysis can be ruled out on account of the value 0.0015 at 25° for the constant of limiting hydrolysis in acid solution.[4]

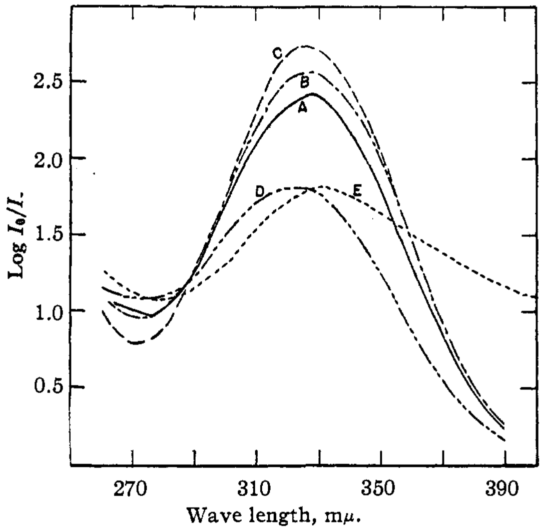
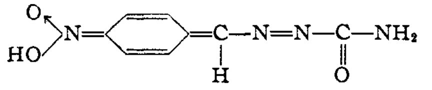


Fig. 2.—Ultraviolet absorption spectrum of *p*-nitrobenzaldehyde semicarbazone in aqueous solution: A, *p*H 1.3; B, *p*H 2.5; C, *p*H 5.7; D, *p*H 9.5; E, *p*H 11.3.

The effect of *p*H on the ultraviolet absorption spectrum of *p*-nitrobenzaldehyde semicarbazone is illustrated in Fig. 2. An isobestic point occurs at about 287 mμ. The wave length of the absorption maximum remains at about 325 mμ but at *p*H 11.3 a shift of 5 mμ toward the red is observed. The isobestic point indicates a change in the molecular structure with a change in *p*H. We suggest for the tautomeric form a quinonoid structure



Such a structure can explain also the solubility in alkaline solution of this, and other aromatic nitro-aldehyde semicarbazones (such as *o*-nitrobenzaldehyde and 5-nitro-2-furfuraldehyde), and the insolubility of *m*-nitrobenzaldehyde semicarbazone.

The spectrum in 1 *N* hydrochloric acid solution shows a new band at 267 mμ, the band at 287 mμ being reduced to an inflection.

On standing in alcoholic solution, the absorption spectrum of *p*-nitrobenzaldehyde semicarbazone showed a drop in intensity and a shift toward the shorter wave length (331 mμ → 320 mμ), probably due to a *cis–trans* rearrangement. The Fisher–Hirschfelder–Taylor models suggest that the *cis* isomer cannot assume a planar configuration, due to steric hindrance between the secondary nitrogen atom and the ortho hydrogens.

On crystallization from water, *p*-nitrobenzaldehyde semicarbazone may separate in a white or a yellow form, depending upon conditions. These forms have been studied in a polarizing microscope. The yellow form is needle-like, with an extinction angle of 44°; the white form appeared in rectangular crystals, which showed practically no extinction when the microscope stage was turned

[2] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[3] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 289.

[4] J. B. Conant and P. D. Bartlett, THIS JOURNAL, **54**, 2881 (1932).

360°, the nicols being crossed. The crystals were bi-axial, section perpendicular to an optical axis; the isogyra was practically straight at rotation of the section. The angle between the optical axis must be nearly 90°; optically +.

Experimental

The aldehydes and the semicarbazones have been prepared by the usual methods. The latter were recrystallized from water and dried in a vacuum desiccator over calcium chloride. A solution of approximately 100 mg. per liter of benzaldehyde semicarbazone was prepared and solutions at different *p*H values were obtained by adding 2 cc. of the above solution in a 25 cc. volumetric flask and filling up with distilled water and acid (HCl, 1 *N*) or base (NaOH, 1 *N*).[5] A similar procedure was used with the *p*-nitro derivative.

Spectral measurements were carried out in a Beckman D. U. Quartz Spectrophotometer, using 1 cm. silica cells.

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[5] The *p*H's were checked with a potentiometer.

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Melting Point of Magnetite–Silica Mixtures in Air

BY L. S. DARKEN

In commenting on my recent paper, "Melting Points of Iron Oxides in Contact with Silica,"[1] one of the referees questioned the value (1442°) reported there for the melting point of magnetite–silica mixtures in air. Such question arises naturally from several statements in the literature. For example, Bowen and Schairer[2] found "no more than a little liquid" formed by heating mixtures of iron oxide and silica to temperatures approaching 1500°, even in a vacuum furnace. Cook[3] observed fusion of magnetite–silica mixtures only near and above 1600°.

An attempt was made to resolve this apparent discrepancy by determining the approximate melting point by a more common method, namely, to prepare an intimate mixture of magnetite and silica by a preliminary fusion and then to determine the melting point of the mixture. Equal weights of magnetite and quartz were mixed by grinding in a mortar to pass a 400-mesh sieve. The mixture was placed in a small (1 ml.) platinum crucible and heated in an air atmosphere in a tubular "Globar" furnace. Starting at 1540° it was held at each of successively higher temperatures for fifteen minutes, being removed and examined in between. This procedure was continued until 1680° (near the limiting temperature of furnace) was reached, at which temperature the charge had sintered only slightly and was easily broken by gentle tapping or probing with a needle.

The failure to obtain a premelt by the above method was somewhat surprising: In order to avoid a large excess of silica another method was tried. A 2-cm. length of clear vitreous silica rod was placed vertically in the crucible and surrounded with magnetite (the same used by Darken and Gurry[4]). This charge was then heated in air to slightly above the melting point of magnetite (1597°) and held there one hour. The molten oxide was thus undoubtedly saturated, or nearly saturated, with silica. The charge was cooled and removed from the crucible; the silica rod and adjacent portions of the melt were discarded.

Having thus obtained a fused intimate mixture of magnetite and silica the melting point was determined as follows: The finely crystalline massive oxide was broken into small pieces about 3 mm. across. One of these pieces was placed in a platinum wire helix[5] and held about ten minutes at a predetermined temperature in an air atmosphere in the furnace. If extensive melting occurred the molten oxide ran down the helix and adhered to the lowest convolution. If no melting occurred the sharp corners and edges of the broken piece were still visible after cooling. From a series of such tests it was found that melting did occur at 1455 ± 5° but did not occur 20° lower. No attempt was made to establish closer limits.

Thus the difficulty in melting the mechanical mixture confirms the reports of Bowen and Schairer and of Cook, whereas the determination of the melting point by remelting confirms roughly the results of my previous investigation which placed the melting point at 1442°.

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[1] L. S. Darken, THIS JOURNAL, **70**, 2046 (1948).

[2] Bowen and Schairer, *Am. J. Sci.*, **24**, 177 (1932).

[3] W. J. Cook, *J. Am. Ceram. Soc.*, **22**, 322 (1938).

[4] Darken and Gurry, THIS JOURNAL, **68**, 798 (1947).

[5] The platinum helix was previously loaded with the oxide and held near 1500° for several hours so that the surface would absorb sufficient iron to be in substantial equilibrium with the melt. This precaution was taken lest the platinum absorb sufficient iron from the test specimen to seriously lower the iron–oxygen ratio to a value below that corresponding to the gas equilibrium.

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RECEIVED JANUARY 3, 1949

Standard Potential of the Mercury–Mercury(I) Phosphate Electrode

BY THOMAS DE VRIES AND DONALD COHEN

A study was made of the mercury–mercury (I) phosphate electrode in phosphoric acid solutions of various concentrations with cells of the type: H_2, H_3PO_4 (*m*), Hg_2HPO_4 (s), Hg. There is very little information in the literature about mercurous phosphate. Gerhardt[1] in 1849 and Haack[2] in 1891 had prepared mercurous orthophosphate by adding a solution of mercurous nitrate to an excess of sodium phosphate solution. They obtained a white or yellow precipitate. Latimer and Hildebrand[3] give the formula of the orthophosphate as $Hg_6(PO_4)_2$.

Experimental

Mercurous Phosphate.—Mercury(I) nitrate was dissolved in water acidified with nitric acid. This solution was slowly added at room temperature to a solution of primary sodium phosphate, NaH_2PO_4, present in excess. A fine white precipitate first formed and gradually changed to a pale yellow or even a deep yellow color. The temperature at which the precipitation was carried out had no effect on the color. Analysis indicated the yellow compound to be the tertiary phosphate, Hg_3PO_4.

Anal. Calcd. for Hg_3PO_4: Hg, 85.21. Found: Hg, 85.41, 85.50.

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[1] Gerhardt, *Jahresber.*, 288 (1849).

[2] Haack, *Ann.*, **262**, 192 (1891).

[3] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1940.