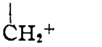
difference between cyclopentyl and cyclopropyl halides on this score.

The moment observed for cyclopropylidene chloride is about 0.3D below that for cyclopentylidene chloride and 0.2D below that for isopropylidene chloride.[24] This indicates again that there may be a small contribution in the cyclopropyl compound from structures placing a positive charge on the chlorine atoms. The moments observed for vinylidene chloride,[25] 1.18D, and 1,1-dichloropropene-1,[23] 1.73D, are 1.0D and 0.45D, respectively, lower than isopropylidene chloride. It is interesting to note that the moments of cyclopropylidene, cyclopentylidene and isopropylidene chlorides are larger than the respective monochlorides although one might expect the reverse to be true from the relative magnitudes of the moments of the methylene and methyl halides.

The moment of cyclopropyl cyanide, 3.75D, is 0.04D higher than cyclopentyl cyanide and 0.14D higher than isopropyl cyanide.[5] This may indicate a small contribution from structures



$$\begin{array}{l}CH_2—CH{=}C{=}N:^-\\ |\\ CH_2^+\end{array}$$

tending to increase the moment, just as in benzonitrile, which shows an increase of about 0.25D due to conjugation. However, it must be observed that no great confidence can be placed in the interpretation of these moments since vinyl cyanide shows a decrease of about 0.1 to 0.2D below the aliphatic cyanides both in vapor[26] and solution.[5] The increase might be due entirely, or in part, to effects of induction.

A comparison of the cyclopentyl compounds with the corresponding *s*-butyl or isopropyl derivatives indicates that the observed moments are normal. Thus, in benzene solution the moment observed for *s*-butyl chloride is 2.09[27]; for *s*-butyl bromide, 2.12[27]; for *s*-butyl iodide, 2.04[27]; for isopropylidene chloride, 2.18[24]; and for isopropyl cyanide, 3.61.[5] The greater polarizibility of the cyclopentane ring, and the fact that a larger portion of polarizable matter is held near to the line of the original dipole, would tend to make the contribution from induced dipoles larger in the cyclopentyl compounds and so the observed moments should be slightly larger and indeed small increases are occasionally observed. The moment of cyclopentyl fluoride is the first value to be reported for a secondary fluoride and, as would be anticipated, falls between those observed for *n*-amyl and *t*-amyl fluorides.[5]

Summary

The dipole moments of cyclopropyl chloride and 1,1-dichlorocyclopropane in benzene solution have been shown to be about 0.3D less than the corresponding cyclopentyl compounds. This has been interpreted as indicating a small contribution from ionic resonance structures analogous to the principal ionic resonance structures in vinyl chloride and chlorobenzene.

The dipole moments of the cyclopentyl halides and cyanide are close to those of the corresponding secondary aliphatic compounds.

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[24] Gross, *Physik. Z.*, **32**, 587 (1931); **33**, 719 (1932).

[25] Errera, *ibid.*, **27**, 764 (1926).

[26] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

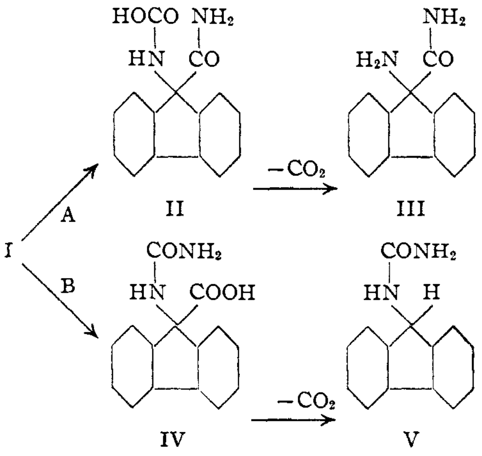
[27] Parts, *Z. physik. Chem.*, **B7**, 327 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE WM. S. MERRELL CO.]

The Alkaline Hydrolysis of Fluorenone-spirohydantoin

BY G. H. HARRIS,[1] B. R. HARRIMAN[2] AND KEITH W. WHEELER

Mild hydrolysis of fluorenone-spirohydantoin (I) might be expected to proceed along one of two possible courses, as A or B, below. There are numerous cases reported in the literature[3] in which hydrolysis of other hydantoins in the presence of barium hydroxide leads to substituted hydantoic acids. In these cases the hydrolysis follows course B and compounds of the type illustrated by (IV) are isolated. In other cases wherein hydrolysis leads to an amine, the same product would result from either course.



It has been reported[4] that hydrolysis of fluoren-

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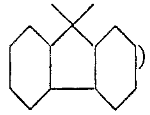
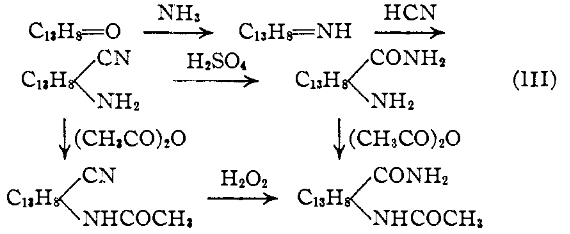
[3] Baeyer, *Ann.*, **130**, 160 (1864); Bailey, *Am. Chem. J.*, **28**, 395 (1902); Biltz and Heyn, *Ber.*, **45**, 1672 (1912); Heintz, *Ann.*, **169**, 128 (1873); Klason, *Chem. Ztg.*, **14**, 200 (1891); Pinner, *Ber.*, **21**, 2321 (1888); Pinner and Spilker, *ibid.*, **22**, 687 (1889); Urech, *Ann.*, **164**, 264 (1872); West, *J. Biol. Chem.*, **34**, 191 (1918); Wheeler and Hoffman, *Am. Chem. J.*, **45**, 373 (1911).

[4] McCown and Henze, THIS JOURNAL, **64**, 689 (1942).

one-spirohydantoin in the presence of barium hydroxide leads to 9-amino-9-carbamylfluorene (III), although the product obtained did not show the reactions expected for a compound of this structure; it did not give a positive carbylamine reaction, did not react with nitrous acid, and did not dissolve in cold dilute or concentrated hydrochloric acid. Furthermore, the isomeric compound, 9-fluorenylurea (V), is reported[5] as melting at 255°, which is practically the same melting point as that reported by McCown and Henze for the product they obtained (254–256°).

We have found that the hydrolysis of fluorenone-spirohydantoin (I) does indeed lead to 9-fluorenylurea instead of 9-amino-9-carbamylfluorene.[5a] The hydrolysis as described by McCown and Henze was repeated and the product obtained gave no depression in melting point when mixed with 9-fluorenylurea prepared from 9-aminofluorene and potassium cyanate. The isomeric compound (III) was successfully prepared by the following series of reactions ($C_{13}H_8$ represents the fluorenylidene radical, )



$$C_{13}H_8{=}O \xrightarrow{NH_3} C_{13}H_8{=}NH \xrightarrow{HCN}$$

$$C_{13}H_8\genfrac{}{}{0pt}{}{CN}{NH_2} \xrightarrow{H_2SO_4} C_{13}H_8\genfrac{}{}{0pt}{}{CONH_2}{NH_2} \quad (III)$$

$$\downarrow (CH_3CO)_2O \qquad\qquad \downarrow (CH_3CO)_2O$$

$$C_{13}H_8\genfrac{}{}{0pt}{}{CN}{NHCOCH_3} \xrightarrow{H_2O_2} C_{13}H_8\genfrac{}{}{0pt}{}{CONH_2}{NHCOCH_3}$$

The product (III) was found to have characteristics entirely different from those of the product from the hydrolysis of fluorenone-spirohydantoin. The acetyl derivative of (III), prepared by two different procedures, was likewise different from the acetyl derivative of the hydrolysis product. The acetyl derivatives of the hydrolysis product and of 9-fluorenylurea were identical. The products from the reaction of aniline with the hydrolysis product and with 9-fluorenylurea were identical, whereas aniline did not react with (III) under similar conditions.

We were unable to transform 9-amino-9-cyanofluorene into 9-amino-9-carbamylfluorene by means of hydrogen peroxide (Radziszewski reaction) although the reaction was successfully applied to 9-acetamino-9-cyanofluorene.

Acknowledgment.—We wish to express our appreciation to Miss Betty Lee Denman for technical assistance on certain phases of the experimental work.

Experimental

All melting points are corrected.

9-Fluorenylurea.—9-Aminofluorene hydrochloride, from the reduction of fluorenone oxime,[6] was converted to 9-fluorenylurea by reaction with potassium cyanate. After recrystallization from ethanol, the white needles melted at 256–257°.[5]

Anal.[7] Calcd. for $C_{14}H_{12}ON_2$: C, 74.98; H, 5.40; N, 12.50. Found: C, 75.02; H, 5.47; N, 12.26.

The hydrolysis of fluorenone-spirohydantoin was carried out according to McCown and Henze,[4] and a product melting at 255–257° was obtained. When an equal quantity of this product was mixed with authentic 9-fluorenylurea, the mixture melted at 255–257°.

sym.-**9-Fluorenylphenylurea.**—9-Fluorenylurea (3.0 g.) and aniline (20 ml.) were heated to refluxing for two hours. The cooled mixture was triturated with 10% hydrochloric acid, leaving an 85% yield of crude product. For analysis, the material may be recrystallized from a large volume of glacial acetic acid or ethanol, giving white felted needles, of m. p. 297–298°[8] (sealed tube).

Anal. Calcd. for $C_{20}H_{16}ON_2$: C, 79.98; H, 5.37; N, 9.33. Found: C, 80.00; H, 5.18; N, 9.14.

The product from the hydrolysis of fluorenone-spirohydantoin was treated with aniline in a similar manner, and the resulting material showed no depression in melting point when mixed with authentic *sym.*-9-fluorenylphenylurea.

sym.-**9-Fluorenylacetylurea.**—Three grams of 9-fluorenylurea was added to a solution of 15 ml. of acetyl chloride in 100 ml. of glacial acetic acid and the solution was heated on the steam-bath for twelve hours. The precipitated white needles were collected and washed thoroughly with acetic acid, water and finally alcohol. The material melted to a cloudy liquid at about 255°, resolidified and melted again at about 303°. The yield was 65%.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30; N, 10.52. Found: C, 72.07, 72.11; H, 5.31, 5.25; N, 10.61, 10.57.

The product from the hydrolysis of fluorenone-spirohydantoin was treated with acetyl chloride in a similar manner, and an identical product was obtained.

Fluorenylideneimine.—A simplified procedure based on the action of ammonia gas upon molten fluorenone has been developed for the preparation of this compound. One hundred grams of fluorenone in a three-necked, round-bottomed flask was maintained at 165° in an oil-bath while anhydrous ammonia gas was bubbled in for five hours. The cooled reaction mixture was dissolved in ether and gaseous hydrogen chloride was passed in until the solution was acidic to congo red paper. The precipitated imine hydrochloride was filtered, washed with ether, decomposed by aqueous ammonia and the liberated imine then taken up in petroleum ether (b. p. 75–90°). The solution was decolorized with charcoal and upon cooling deposited pale yellow needles of m. p. 124–124.5°. The yield of 25 g. corresponded to 66% based on the fluorenone reacting, since 62 g. of fluorenone was recovered from the original ether filtrate. Part of the imine was converted to the hydrochloride for analysis.

Anal. Calcd. for $C_{13}H_{10}NCl$: Cl, 16.4. Found: Cl, 16.3.

This compound has previously been prepared from fluorenone and ammonia, by allowing the mixture to react at room temperature for several weeks.[9]

9-Amino-9-cyanofluorene.—To 18 g. of fluorenylideneimine in 800 ml of absolute ether was added 30 ml. of liquid hydrogen cyanide. The solution was allowed to

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(5) Kerp, *Ber.*, **29**, 231 (1896). Schmidt and Stutzel, *Ber.*, **41**, 1248 (1908), claim that 9-fluorenylurea does not melt up to 300°.

(5a) The manuscript of this paper was read by Professor H. R. Henze, who has accepted the experimental evidence and concurs in this conclusion.

(6) Ingold and Wilson, *J. Chem. Soc.*, 1499 (1933).

(7) All single analyses by Dr. Carl Tiedcke, New York. Duplicate analyses by Dr. E. W. D. Huffman, Denver, Colo.

(8) Schmidt and Stutzel, *Ber.*, **41**, 1248 (1908), report that this compound decomposed at about 310°. They prepared it from 9-aminofluorene and phenyl isocyanate.

(9) Pinck and Hilbert, THIS JOURNAL, **56**, 490 (1934).

stand in a stoppered flask at room temperature for one week. Most of the ether and excess hydrogen cyanide were then boiled off. The residue was crystallized from a mixture of ether and petroleum ether, giving 12 g. of pale yellow crystals, melting at 94–95° and corresponding to a yield of 58%. A yield of 70% was obtained from a larger run, using 203 g. of fluorenylideneimine and 400 ml. of hydrogen cyanide. The analytical sample was recrystallized twice more from the same solvent, and melted at 95–96°.

Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.52; H, 4.89; N, 13.59. Found: C, 81.47, 81.55; H, 4.95, 4.90; N, 13.58, 13.46.

9-Acetamino-9-cyanofluorene.—When 11 g. of acetic anhydride was added to 20.6 g. of 9-amino-9-cyanofluorene dissolved in 39 ml. of pyridine, an exothermic reaction occurred, and crystals began to precipitate within a short time. The mixture was allowed to stand overnight, then 150 ml. of water and 10 ml. of concentrated hydrochloric acid were added. The precipitate was collected and recrystallized from ethanol. A yield of 21 g. or 85% was obtained. The long white flakes melted at 228–229°.

Anal. Calcd. for $C_{16}H_{12}ON_2$: C, 77.38; H, 4.87; N, 11.29. Found: C, 77.45; H, 4.82; N, 11.63.

9-Amino-9-carbamylfluorene (III).—To 100 ml. of concentrated sulfuric acid was added slowly 40 g. of finely powdered 9-amino-9-cyanofluorene, with cooling and stirring. The viscous red solution was allowed to stand at room temperature for forty-eight hours. It was then poured onto 250 g. of finely crushed ice, and finally neutralized with ammonia. The precipitate was collected, washed, and recrystallized from a 50–50 mixture of aqueous ethanol. A yield of 25.5 g., or 59%, of white crystals melting at 147–148° was obtained. The analytical sample after two more recrystallizations melted at 150–151°.

Anal. Calcd. for $C_{14}H_{12}ON_2$: C, 74.98; H, 5.40; N, 12.50. Found: C, 74.78; H, 5.38; N, 12.65.

This compound gave a positive carbylamine test when treated with chloroform and sodium hydroxide. It is readily soluble in alcohol and dioxane, moderately soluble in benzene, and readily soluble in cold 10% hydrochloric acid.

An attempt to prepare this compound by a Radziszewski reaction, as modified by Murray and Cloke,[10] on 9-amino-9-cyanofluorene was unsuccessful. The products isolated from the reaction were fluorenone and 9-carbamylfluorene, m. p. 257–258°.[11] The melting point of a mixture of the latter with 9-fluorenylurea was 230–235°.

Likewise, attempts to deacetylate 9-acetamino-9-carbamylfluorene were unsuccessful. Alcoholic ammonia at room temperature for two weeks was without effect. Alcoholic ammonia with added ammonium iodide in an autoclave at 120° for twelve hours gave only 9-acetaminofluorene, of m. p. 264–265°. Melting point of a mixture of this with authentic 9-acetaminofluorene prepared from 9-aminofluorene showed no depression. Alcoholic sodium hydroxide under reflux for two hours gave as a principal product, 9-acetaminofluorene, and a small amount of 9-aminofluorene.

9-Amino-9-carbamylfluorene did not react with aniline after three hours of refluxing. A recovery of about 75% of the starting material was obtained.

9-Acetamino-9-carbamylfluorene.—This compound was prepared both from 9-amino-9-carbamylfluorene and from 9-acetamino-9-cyanofluorene.

Ten grams of 9-amino-9-carbamylfluorene, 6 ml. of acetic anhydride and 20 ml. of pyridine were mixed, whereupon an exothermic reaction occurred. After standing overnight, an excess of 10% hydrochloric acid was added and the precipitate was collected. Ten grams of crude product was obtained. It was recrystallized from ethanol, giving 7.7 g., or a yield of 65%. The colorless hexagonal rods melted at 215.5–216°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30; N, 10.52. Found: C, 72.22, 72.17; H, 5.39, 5.37; N, 10.41, 10.54.

The Radziszewski reaction as modified by Murray and Cloke[10] was successfully applied to 9-acetamino-9-cyanofluorene. The latter compound (9 g.) and 100 ml. of 30% hydrogen peroxide were mixed, and sufficient acetone to produce a homogeneous solution was added. Then 12 ml. of 10% sodium carbonate solution was added, and the solution was allowed to stand at room temperature for four days. Most of the acetone was removed on the steam-bath, and the residue was recrystallized from ethyl acetate containing about 5% ethanol. A yield of 6.6 g., or 68.5%, of material melting at 212–214° was obtained. The analytical sample was recrystallized twice more and melted at 214–215°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30; N, 10.52. Found: C, 72.09, 72.18; H, 5.34, 5.38; N, 10.39, 10.42.

A mixture of the materials from the two different preparations melted at 214–216.5°.

Summary

It has been shown that the product obtained upon hydrolysis of fluorenone-spirohydantoin in the presence of barium hydroxide is 9-fluorenylurea instead of 9-amino-9-carbamylfluorene as previously reported. The latter compound was prepared from 9-amino-9-cyanofluorene, which in turn was obtained from the addition of hydrogen cyanide to fluorenylideneimine.

A number of new derivatives of fluorene were prepared and characterized.

CINCINNATI, OHIO RECEIVED JANUARY 25, 1946

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[10] Murray and Cloke, THIS JOURNAL, **56**, 2749 (1934).

[11] Stollé and Wolf, *Ber.*, **46**, 2248 (1913), give m. p. 251°.