5-Phenylpentanol from Run 8, b. p. 142–148° at 10 mm., d^{26}_4 0.9857, had the characteristic odor of lemons and compared favorably with the product as previously described, b. p. 140–142° at 16 mm., d^{26}_4 0.9651.[15] Since no direct derivatives were found, the alcohol was converted into crude 5-phenylpentyl bromide by refluxing with hydrobromic acid containing a trace of sulfuric acid. The bromide was refluxed in ethanol with an equivalent of ammonium dithiocarbamate[16] to produce an oil which upon crystallization from ether–petroleum ether gave 5-phenylpentyl dithiocarbamate, m. p. 72–74°, lit.[17] 75°.

Summary

1. In acid solution it is not practical to selectively hydrogenate allyl or methallylbenzyl ethers over palladium–charcoal.

2. The structures of certain aryldioxanes have been proved by hydrogenation.

3. Some compounds isomeric with 2,3-diphenyldioxane do not react with hydrogen in ways consistent with their suspected structures.

4. A convenient synthesis of 5-phenylpentanol has been described.

EVANSTON, ILLINOIS RECEIVED DECEMBER 11, 1947

---

(15) v. Braun, Anton and Weissbach, *Ber.*, **63**, 2847 (1930); v. Braun, *ibid.*, **44**, 2867 (1911).

(16) Mulder, *Ann.*, **168**, 228 (1873).

(17) v. Braun, *Ber.*, **45**, 1563 (1912).

[CONTRIBUTION FROM THE LABORATORY OF RADIOCHEMISTRY, UNIVERSITY OF CINCINNATI]

3-Nitrofluorenone

BY FRANCIS EARL RAY AND JAMES G. BARRICK

Mononitration of fluorene yields only 2-nitrofluorene. As this is easily oxidized to 2-nitrofluorenone the properties of both compounds are well known.[1]

4-Nitrofluorenone also seems to be well known, having first been prepared by Schmidt and Baur,[2] from the known 4-nitrophenanthraquinone by means of the benzilic acid rearrangement followed by oxidation and decarboxylation. Courtot[3] and Bell[4] have confirmed this work.

1-Nitrofluorenone has not been prepared.

3-Nitrofluorenone was first reported by Schmidt and Soll[5] who obtained it by the simultaneous nitration and oxidation of 9,10-diaminophenanthrene to 3-nitrophenanthraquinone. A benzilic acid rearrangement, followed by oxidation and decarboxylation gave a compound melting at 209–210° which was described as 3-nitrofluorenone. Its oxime melted at 240°. As the structure of 3-nitrophenanthraquinone had been proved conclusively by J. Schmidt[6] seven years previously, there seemed no reason to question the identity of Schmidt and Soll's compound. Especially was this true after the appearance of the paper by Eckert and Langecker[7] in 1928.

Using a different method, the simultaneous nitration and oxidation of 2-acetylaminofluorene to 3-nitro-2-amino-fluorenone followed by removal of the 2-amino group, Eckert and Langecker obtained identical melting points, Table I. Eckert and Langecker proved the position of the nitro group by converting their compound to the known 3-hydroxyfluorenone.[8]

Better evidence for the identity of 3-nitrofluorenone could hardly be desired. Nevertheless, in 1931 Bardout[9] reported that his preparation of this compound by essentially Eckert and Langecker's method yielded 3-nitrofluorenone melting, not at 210°, but at 239°. The oxime instead of melting at 240°, as previously reported, melted at 221°, cor. Bardout also converted his compound to the known 3-hydroxyfluorenone as well as to the known 3-bromofluorenone.[10]

In the course of his synthesis Bardout also obtained 3-nitrofluorene melting at 105°. Hayashi and Nakayama[11] repeated the synthesis of 3-nitrofluorene and found the same melting point as Bardout. They did not, however, oxidize it to the fluorenone.

With a view to resolving this difficulty, Scheer[12] attempted to repeat Bardout's synthesis but found great difficulty in isolating pure compounds. Repeating Schmidt and Soll's work, he obtained, supposedly, 3-nitrofluorenone which melted considerably higher than Schmidt and Soll's and Eckert and Langecker's compound but not quite as high as Bardout's. From the two degree range in melting point Scheer concluded that his material was still impure. The significant part remains that even the impure material melted considerably higher than the first investigators reported. A summary of these results will be found in Table I.

It seemed of interest, therefore, to attempt an entirely *new* synthesis of 3-nitrofluorenone in the hope of settling the controversy.

Our starting material was the readily available 2-aminobiphenyl. This was treated with toluenesulfonyl chloride and the product nitrated accord-

---

(1) "Organic Syntheses," Coll. Vol. II, 447 (1943); Barbier, *Ann. chim. phys.*, [5] **7**, 479 (1876); Ullmann and Mallett, *Ber.*, **31**, 1694 (1898).

(2) Schmidt and Baur, *Ber.*, **38**, 3737 (1905).

(3) Courtot, *Ann. chim.*, [10] **14**, 5 (1930).

(4) Bell, *J. Chem. Soc.*, 1990 (1928).

(5) Schmidt and Soll, *Ber.*, **41**, 3691 (1908).

(6) J. Schmidt, *ibid.*, **34**, 3531 (1901).

(7) Eckert and Langecker, *J. prakt. Chem.*, **118**, 263 (1298).

(8) Ullmann and Bleier, *Ber.*, **35**, 4279 (1902); Errera and La Spada, *Gazz. chim. ital.*, **35**, 539 (1905).

(9) Bardout, *Anales asoc. quim. argentina*, **19**, 117 (1931); **22**, 123 (1934).

(10) Montagne, *Rec. trav. chim.*, **28**, 449 (1909); Montagne and van Charenti, *ibid.*, **32**, 164 (1913).

(11) Hayashi and Nakayama, *J. Soc. Chem. Ind. Japan*, **36**, 1278 (1933).

(12) Scheer, Master's Thesis, University of Cincinnati, 1942.

TABLE I

PROPERTIES OF 3-NITROFLUORENONE AND DERIVATIVES

Worker	Melting points, °C.		3-Amino- fluorenone	Acetyl deriv.
	Ketone	Oxime		
S and S[5]	209–210	240		
E and L[7]	210	240	158–159	215
Bardout[9]	232 (239 cor.)	217 (221 cor.)		
Scheer[12]	225–227	214		
Authors	235–236 (239–240 cor.)	224–225	157–158	215–216

ing to the method of Bell[13] and of Jones and Braker[14] to give on hydrolysis 2-amino-5-nitrobiphenyl. The use of the acetyl derivative gives inferior results in nitration.[15] 2-Cyano-5-nitrobiphenyl was obtained in the usual manner. On hydrolysis, 5-nitrobiphenyl-2-carboxylic acid was obtained.

The structure of this compound rests on Sako's[16] proof of structure for 2-amino-5-nitrobiphenyl. Reduction gave the diaminobiphenyl and by conversion to a Lauth's violet, the amino groups were shown to be *para* to each other. An isomeric diamine was shown to be 2,3-diaminobiphenyl by treating it with phenanthraquinone to form the quinoxaline. The 2-amino-4-nitro isomer would yield the well known 2-nitrofluorenone.

5-Nitrobiphenyl-2-carboxylic acid was converted to 3-nitrofluorenone by heating with concentrated sulfuric acid, a method widely used in the preparation of fluorenones[17] as well as other cyclic ketones.[18] The crude 3-nitrofluorenone was obtained on pouring the sulfuric acid solution onto ice. The oxime was prepared by Bardout's method. It melted somewhat higher than Bardout's value but not nearly as high as the value reported by Schmidt and Soll, and by Eckert and Langecker, Table I.

It is possible that the differences in the melting point of the oximes may be due to *cis–trans* isomerism. It is not so easy, however, to explain the low melting point for 3-nitrofluorenone reported by the earlier investigators. If only a single paper were involved one might be tempted to suggest that the melting point values for the ketone and the oxime were interchanged.

In the hope of obtaining further data we reduced our 3-nitrofluorenone to 3-aminofluorenone and prepared the acetyl derivative. Much to our surprise we found the melting points to agree almost exactly with those reported by Eckert and Langecker. We must conclude that the impurities in their 3-nitrofluorenone were eliminated when it was converted into 3-aminofluorenone. These values are also given in Table I.

Experimental

2-Aminobiphenyl.—This dark pink material was Eastman Kodak Co. practical grade and melted at 47–49°. Distillation under reduced pressure removed the color but did not raise the melting point above 49°.

2-*p*-Toluenesulfonamidobiphenyl.—This compound was best prepared by condensing *p*-toluenesulfonyl chloride and 2-aminobiphenyl in the presence of pyridine. From 85 g. of 2-aminobiphenyl, 100 g. of *p*-toluenesulfonyl chloride and 200 cc. of pure pyridine there was obtained 135 g. (84%) of 2-*p*-toluenesulfonamidobiphenyl melting at 98–99°.[14]

5-Nitro-2-*p*-toluenesulfonamidobiphenyl.—Bell's method[13] gave largely the unchanged starting material. It was modified as follows. Sixty grams of 2-*p*-toluenesulfonamidobiphenyl was dissolved in 120 cc. of warm glacial acetic acid, nitric acid (15 cc., sp. g. 1.5) was added slowly and the mixture was heated on the steam-bath to 90°. When the temperature started to rise rapidly, the beaker was removed from the heat and the reaction allowed to continue for three minutes. It was poured into cold water and a red oil precipitated which quickly solidified. When recrystallized from 400 cc. of hot ethyl alcohol, yellow needles were obtained melting at 168–169°; yield 55 g. (80%). When recrystallized a second time the compound melted sharply at 169°.

5-Nitro-2-aminobiphenyl.—A solution of 25 g. of 5-nitro-2-*p*-toluenesulfonamidobiphenyl in 50 cc. of concentrated sulfuric acid was allowed to stand for one hour at room temperature. It was then added dropwise to 200 cc. of an ice slurry. The yellow amine weighed 16 g. (yield quantitative) and was recrystallized twice from alcohol, m. p. 125°.[13]

5-Nitro-2-cyanobiphenyl.—A solution of 16 g. of 5-nitro-2-aminobiphenyl in 100 cc. of concentrated hydrochloric acid was diazotized at 0° with 5.2 g. of sodium nitrite in 50 cc. of water. After one hour urea was added and the solution filtered. This solution was slowly added to a solution of potassium cuprocyanide, prepared from 25 g. of copper sulfate and 28 g. of potassium cyanide and containing 15 g. of sodium carbonate, at 10°. After half of the diazonium solution had been added a further 15 g. of sodium carbonate was added in 50 cc. of water. After one hour the light tan precipitate was removed. It weighed 12 g.; yield, 72%. On recrystallization it melted at 134–135°.[13]

5-Nitrobiphenyl-2-carboxylic Acid.—Twelve grams of 5-nitro-2-cyanobiphenyl was hydrolyzed by boiling with 70 cc. of concentrated sulfuric acid in 100 cc. of water for six hours. After several hours the solid changed to an oil and finally became semisolid. The crude material (10 g.) was dissolved in 100 cc. of 10% sodium hydroxide, 1 g. of Darco added, the mixture boiled for fifteen minutes, filtered and acidified. White platelets weighing 6 g., yield 50%, were obtained melting at 179–180°. Recrystallization from alcohol gave a m. p. of 180°. No m. p. is given by Jones and Braker.[14]

Anal. Calcd. for $C_{13}H_9NO_4$: eq. wt., 243. Found: eq. wt., 244.

3-Nitrofluorenone.—Two grams of 5-nitrobiphenyl-2-carboxylic acid in 10 cc. of concd. sulfuric acid was heated in an oil-bath to 120° and held at this temperature for ten minutes. After cooling this blood red solution to room temperature it was poured into a slurry of ice yielding a yellow precipitate weighing 2 g. It was recrystallized from glacial acetic acid with Darco, then from ethyl alcohol and melted constantly at 235–236° (239–240°, cor.). The same melting point was obtained when samples were recrystallized from benzene and pyridine.

Anal. Calcd. for $C_{13}H_7NO_3$: N, 6.22. Found: N, 6.45.

3-Nitrofluorenone Oxime.—A 0.5-g. sample of 3-nitrofluorenone was heated with 0.25 g. of hydroxylamine in 15 cc. of alcohol and 0.3 g. of oxime was obtained which on recrystallization from alcohol melted at 224–225°, Table I.

---

[13] Bell, *J. Chem. Soc.*, 2770 (1928).

[14] Jones and Braker, U. S. Patent, 1,922,265, August 15, 1933, 1,976,940, October 16, 1934.

[15] Barrick, Master's Thesis, University of Cincinnati, 1947.

[16] Sako, *Bull. Chem. Soc. Japan*, **9**, 55 (1933).

[17] Huntress, Pfister, 3rd, and Pfister, THIS JOURNAL, **64**, 2845 (1942); Atkinson, *et al.*, *ibid.*, **67**, 1513 (1945).

[18] Johnson, "Organic Reactions," Vol. II, 115 (1944).

3-Aminofluorenone.—Five grams of sodium sulfide was added over a period of two hours to 100 cc. of boiling alcohol containing 1 g. of 3-nitrofluorenone and 2 g. of ammonium chloride. After refluxing for an additional hour it was poured into cold water and extracted with ether. The ether was extracted with dilute hydrochloric acid and on neutralization a deep yellow precipitate was obtained. It was not possible to get a better melting point than 142–146°. Following the procedure of Eckert and Langecker,[7] who encountered similar difficulties, the amine was acetylated. Recrystallization from alcohol gave 3-acetylaminofluorenone.

3-Acetylaminofluorenone was hydrolyzed by boiling with 20% hydrochloric acid. It yielded 3-aminofluorenone, Table I.

Summary

A new synthesis of 3-nitrofluorenone has been described and Bardout's characterization of this compound has been substantially confirmed.

The following melting points, uncorrected unless otherwise stated, have been found for 3-nitrofluorenone and related compounds:

	M. p., °C.
3-Nitrofluorenone	235–236 (239–240, cor.)
3-Nitrofluorenone oxime	224–225
3-Aminofluorenone	157–158
3-Acetylaminofluorenone	215–216

The values of the latter two compounds given by Eckert and Langecker have been confirmed but their values for 3-nitrofluorenone and 3-nitrofluorenone oxime as well as those of Schmidt and Soll are shown to be in error.

CINCINNATI 21, OHIO RECEIVED DECEMBER 3, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Synthesis and Spectrum of 2-Cyclopropylpyridine*

BY RAYMOND P. MARIELLA, LOWELL F. A. PETERSON[1] AND ROBERT C. FERRIS[2]

Some recent work by Klotz[3] has shown that the cyclopropane ring, when adjacent to an olefinic or carbonyl group, produced spectra which could be interpreted in terms of resonance due to hyperconjugation. This effect had also been observed by Carr and Burt,[4] who examined the spectra of compounds in which the cyclopropane ring was in "conjugation" with both a carbonyl group and the benzene ring. From these spectra it was not possible to secure information regarding the extent of conjugation of the cyclopropane grouping alone with the aromatic nucleus.

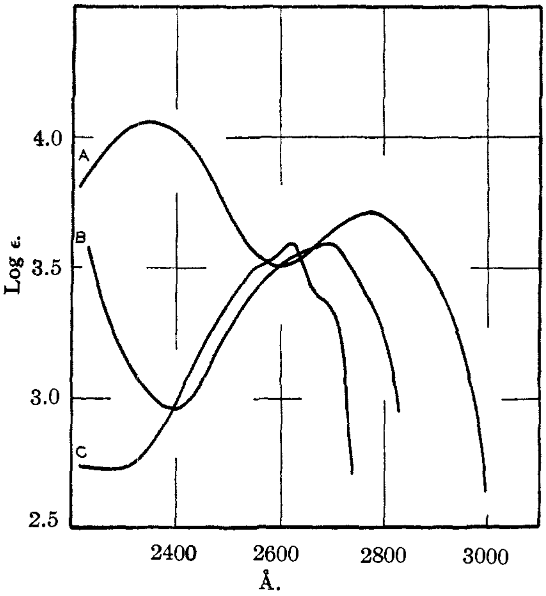

Fig. 1.—Absorption spectra of 2-vinylpyridine, A; 2-cyclopropylpyridine, B; and 2-*n*-propylpyridine, C.

In the present work, 2-cyclopropylpyridine (IX) was synthesized. This compound has the cyclopropane ring alone in conjugation with a highly aromatic nucleus.[5] A comparison of its absorption spectrum with those of 2-*n*-propylpyridine (VIII) and 2-vinylpyridine (X) (Fig. 1), showed the cyclopropane compound to have a maximum (2690 Å.) between that of the similarly conjugated (2775 Å.) and non-conjugated (2620 Å.) system.

Since the maximum for pyridine itself is at 2530 Å.,[6] the presence of an alkyl or alicylic group in the α position causes a shift of the maximum to longer wave lengths. This effect appears greater with the cyclopropyl group than with the *n*-propyl group, and confirms chemical evidence long known[7] that the cyclopropane ring possesses a certain degree of unsaturation. The phenomenon no doubt occurs because the electrons of cyclopropane are rendered especially polarizable by the unusual angle between the bonds.

If the shift to longer wave lengths is to be interpreted as a "hyperconjugation" effect, then in the case of 2-cyclopropylpyridine we can postulate that certain ionic structures exist, which in addi-

---

* Presented before the Division of Organic Chemistry, American Chemical Society, Chicago, Illinois, April 22, 1948.

[1] Present address: Northwestern University Medical School, Chicago, Illinois.

[2] Present address: University of Utah, Department of Chemistry, Salt Lake City, Utah.

[3] Klotz, THIS JOURNAL, **66**, 88 (1944).

[4] Carr and Burt, *ibid.*, **40**, 1590 (1918).

[5] After the initial submission of this manuscript a paper appeared (Rogers, *ibid.*, **69**, 2544 (1947)), in which the absorption spectrum of cyclopropylbenzene was given. This compound also showed a shift in the maximum toward longer wave lengths when compared with propylbenzene, which was interpreted as a hyperconjugation effect.

[6] Fischer and Steiner, *Compt. rend.*, **175**, 882 (1922).

[7] Kohler and Conant, THIS JOURNAL, **39**, 1404, 1699 (1917).