

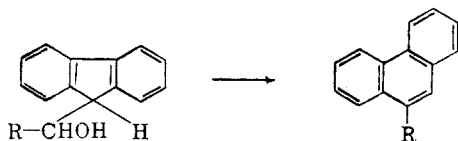
The Pyrolysis of 9-Arylidene- and 9-Alkylidene-fluorenes

S. WAWZONEK, E. DUFEK,¹ AND N. M. SIAL¹

Received October 31, 1955

The pyrolysis of 9-arylidenefluorenes formed fluorene and the corresponding toluene as the main products. A phenanthrene was formed only in the case of 9-benzylidenefluorene. 9-Alkylidenefluorenes upon similar treatment gave fluorene, 9-methylfluorene, and the corresponding 9-alkylfluorene.

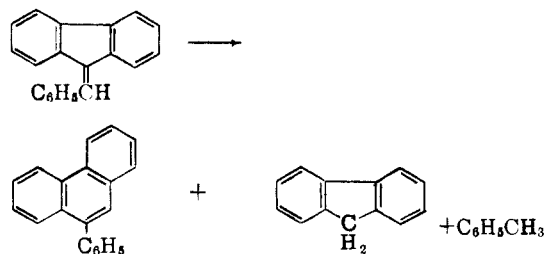
Numerous examples of acid-catalyzed rearrangements of 9-fluorenylcarbinols to the corresponding phenanthrenes have been reported in the literature.² No direct rearrangement of the 9-alkylidene- and 9-arylidene-fluorenes, which could be inter-



mediates in this reaction, has been reported. The simplest member, 9-methylenefluorene, formed by heating 9-methyl-9-hydroxyfluorene at 250° under reduced pressure is reported by Wieland³ to polymerize readily but not to isomerize. The less substituted 1-methyleneindene, obtained in a similar manner from 1-indenylcarbinol by Courtot,⁴ also polymerizes, very readily.

The pyrolysis, using simple atmospheric distillation, of 9-arylidene- and 9-alkylidene-fluorenes has now been studied further as a possible method for preparing substituted phenanthrenes. Introduction of aryl and alkyl groups into the molecule eliminates the possibility of polymerization observed with the simplest member of the series.

The reaction proceeded in the desired fashion only with 9-benzylidenefluorene and gave a 5.5 percent yield of 9-phenylphenanthrene.

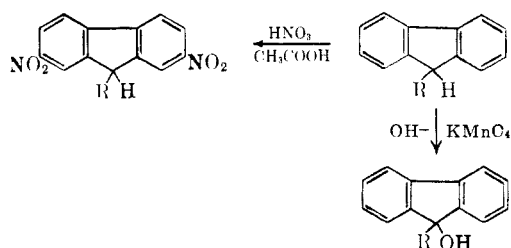


The main reaction was a cleavage of the 9-benzylidenefluorene to fluorene and toluene and suggested the formation of free radicals followed by abstrac-

tion of hydrogen from other molecules. No definite dehydrogenated products were isolated but were probably present in the large amount of carbonaceous material formed.

9-*p*-Methoxybenzylidenefluorene and 9-*p*-chlorobenzylidenefluorene under similar treatment gave only fluorene and the corresponding substituted toluene. The amounts of these compounds obtained from 9-*p*-methoxybenzylidenefluorene were comparable to those obtained for the unsubstituted compound. The pyrolysis of 9-*p*-chlorobenzylidenefluorene differed in that only a trace of fluorene was formed. This reaction was accompanied by the rapid evolution of hydrogen chloride and excessive charring of the compound.

The pyrolysis of 9-ethylidene-, 9-*n*-propylidene-, and 9-*n*-butylidene-fluorene gave no phenanthrenes. The products in each example consisted of a mixture of fluorene, 9-methylfluorene, the corresponding 9-alkylfluorene, and a complex mixture of aliphatic gaseous hydrocarbons. The mixtures of fluorene and alkylfluorenes were separated by fractional distillation and crystallization. Identification of the 9-alkylfluorenes was accomplished either by nitration to the 2,7-dinitro-9-alkylfluorene or oxidation with potassium permanganate to the corresponding 9-alkyl-9-fluorenol.



The absence of 9-ethylfluorene in the pyrolysis products from 9-*n*-propylidenefluorene suggests that the latter compound is cleaved directly to *n*-propyl and ethyl radicals which by decomposition, disproportionation and abstraction of hydrogen give the gaseous products isolated. 9-*n*-Butylidenefluorene in a similar manner must form *n*-butyl and *n*-propyl radicals since no 9-ethylfluorene and 9-*n*-propylfluorene were isolated.

The results obtained are in agreement with observations reported by Wieland⁶ that the distillation

(1) Abstracted in part from the Ph. D. Thesis (1956) of E. Dufek and the M.S. Thesis (1948) of N. M. Sial.

(2) Horning, *Chem. Revs.*, **33**, 89 (1943).

(3) Wieland, Reindel, and Ferrer, *Ber.*, **55**, 3317 (1922).

(4) Courtot, *Ann. chim.*, [9] **4**, 168 (1915).

(5) Wieland and Probst, *Ann.*, **530**, 274 (1937).

of 9-methyl-9-fluorenol from phosphorus pentoxide gave 9-methylfluorene, fluorene, and a polymer. The first two products are probably formed from the intermediate 9-methylene-fluorene and not from the polymer as claimed.

A similar cleavage of alkyl groups would also explain the reported formation of phenanthrene by passing 9-ethylfluorene through a red glowing glass tube.⁶

Cleavages of this type are apparently not restricted to this series but occur also in the Chichibabin preparation of pyridines.⁷

EXPERIMENTAL⁸

Pyrolysis of 9-benzylidene-fluorene. 9-Benzylidene-fluorene⁹ (20 g.) was heated slowly in a distilling flask under nitrogen until the distillation temperature reached 360°. The time required was 25 minutes and represented the end of the formation of volatile products. The distillate (10.5 g.) was separated into three fractions by distillation. The first fraction b.p. 109–113°, was toluene (1.7 g.) and was identified as the 2,4-dinitro derivative, m.p. 70°.

The second fraction, b.p. 135–140° (5 mm.) was recrystallized from methanol and gave fluorene (2.5 g.). Identification was made by comparison with an authentic sample.

The third fraction, 9-phenylphenanthrene, b.p. 215–225° (5 mm.), was recrystallized from methanol and melted at 104–105°; yield 1.1 g. Identification was made by forming a picrate, m.p. 115°, and by comparison with samples prepared from bicyclohexenyl and cinnamic acid¹⁰ and 9-cyclohexenylphenanthrene.¹¹ The latter two samples of 9-phenylphenanthrene melted at 104–105° rather than 113° and 110° as reported and did not lower the melting point when mixed with the sample obtained by pyrolysis. The melting point of 104–105° is in agreement with other reports in the literature.¹²

The residue from the distillation was a red glass which defied crystallization and which could not be separated into any definite compounds by chromatography on alumina.

Pyrolysis of 9-p-anisylidene-fluorene. 9-p-Anisylidene-fluorene (20 g.)⁹ when pyrolyzed by distillation at atmospheric pressure gave 7.5 g. of distillate. No further distillate was obtained by heating at 300° under reduced pressure (10 mm.). Fractionation of the distillate gave p-methoxytoluene (2.6 g.) and fluorene (2.9 g.). The p-methoxytoluene was identified by oxidation to anisic acid, m.p. 184°.

Pyrolysis of 9-p-chlorobenzylidene-fluorene. The pyrolysis of 9-p-chlorobenzylidene-fluorene¹³ (20 g.) gave only 3 g. of distillate. Hydrogen chloride was evolved rapidly from the start of the distillation and excessive charring of the compound took place. Fractional distillation gave p-chlorotoluene (1.5 g.) and fluorene (0.1 g.). The structure of the p-chlorotoluene was demonstrated by oxidation to p-chlorobenzoic acid, m.p. 235°.

2,7-Dinitro-9-alkylfluorenes. The various 2,7-dinitro-9-alkylfluorenes were prepared by the following directions used with 9-methylfluorene.

9-Methylfluorene¹⁴ (2 g.) in glacial acetic acid (10 ml.)

(6) Graebe, *Ber.*, **37**, 4145 (1904).

(7) Eliel, McBride, and Kaufmann, *J. Am. Chem. Soc.*, **75**, 4291 (1953).

(8) Melting points and boiling points are not corrected.

(9) Thiele and Henle, *Ann.*, **347**, 290 (1906).

(10) Weizmann, Bergmann, and Berlin, *J. Am. Chem. Soc.*, **60**, 1331 (1938).

(11) Bergmann and Bergmann, *J. Am. Chem. Soc.*, **59**, 1443 (1937).

(12) Koelsch, *J. Am. Chem. Soc.*, **56**, 480 (1934).

(13) Steglitz, *Ber.*, **52**, 1513 (1919).

(14) Badger, *J. Chem. Soc.*, 535 (1941).

at 5–10° was treated dropwise over a period of 30 minutes with fuming nitric acid (*sp. gr.* 1.50) (10 ml.). The temperature during the addition was kept below 10°. The resulting mixture was heated to 55° and then was cooled. The crystalline product was filtered, washed with cold ethanol (4 ml.), and recrystallized twice from ethyl acetate; m.p. 246–247° dec.; yield 1.1 g. (36.6%).

Anal. Calc'd for C₁₄H₁₀N₂O₄: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.17; H, 3.86; N, 10.46.

2,7-Dinitro-9-ethylfluorene after recrystallization once from benzene and once from ethanol melted at 165° (yield 30.1%).

Anal. Calc'd for C₁₅H₁₂N₂O₄: C, 63.34; H, 4.22; N, 9.85. Found: C, 63.35; H, 4.32; N, 9.83.

2,7-Dinitro-9-n-propylfluorene after one recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°) melted at 163° (yield, 48.9%).

Anal. Calc'd for C₁₆H₁₄N₂O₄: C, 64.45; H, 4.68; N, 9.39. Found: C, 64.52; H, 4.88; N, 9.67.

2,7-Dinitro-9-n-butylfluorene after one recrystallization from ethanol melted at 169–169.5° (yield, 28.6%). The literature reports 163–164°.¹⁵

9-Alkyl-9-fluorenols. The various fluorenols were prepared by the following directions used with 9-methylfluorene.

A mixture of 9-methylfluorene¹⁴ (2 g.) and potassium permanganate (3 g.) in water (160 ml.) containing sodium hydroxide (0.2 g.) was refluxed for 4 hours. The solution was cooled, treated with sodium sulfite (4 g.), and acidified with enough hydrochloric acid to reduce the manganese dioxide formed. The resulting precipitate after recrystallization from benzene and petroleum ether (b.p. 30–60°) melted at 173–174°; yield, 1.6 g. A mixture with a sample prepared from fluorenone and methylmagnesium bromide¹⁶ melted at 173–174°.

9-n-Propyl-9-fluorenol. This compound was prepared by the addition of n-propylmagnesium bromide to fluorenone in a 38.5% yield following the directions used for 9-methyl-9-fluorenol.¹⁶ This compound after two crystallizations from methanol melted at 125–126°.

Anal. Calc'd for C₁₆H₁₆O: C, 85.71; H, 7.14. Found: C, 85.86; H, 7.09.

9-n-Propylidene-fluorene. This compound was prepared in a 58.4% yield by treating 9-n-propyl-9-fluorenol with hydrochloric acid following the directions used for 9-ethylidene-fluorene.¹⁶ Two recrystallizations from methanol gave crystals melting at 44.5–46° and boiling at 150–155° (1 mm.). The literature¹⁷ reports only the boiling point, 155–159° (3 mm.).

Anal. Calc'd for C₁₆H₁₄: C, 93.20; H, 6.79. Found: C, 93.19; H, 6.97.

The picrate crystallized in long yellow needles from methanol.

Anal. Calc'd for C₂₂H₁₇N₃O₇: C, 69.69; H, 3.93; N, 9.65. Found: C, 60.68; H, 4.30; N, 9.58.

9-n-Propylfluorene. 9-n-Propylidene-fluorene (5 g.) in absolute ethanol (50 ml.) was hydrogenated using platinum oxide (0.1 g.) and hydrogen at 40 pounds pressure. Removal of the ethanol followed by distillation gave 4.6 g. of 9-n-propylfluorene; b.p. 126–129° (1 mm.); *n*_D²⁰ 1.6061.

Anal. Calc'd for C₁₆H₁₆: C, 92.30; H, 7.69. Found: C, 91.90; H, 7.75.

9-Ethylfluorene was prepared in the same way and agreed in physical properties with the compound prepared by alkylating sodium fluorenyl with ethyl bromide.¹⁸ 9-n-Butylfluorene¹⁶ prepared in this way was found to melt at

(15) Bachmann and Polansky, *J. Org. Chem.*, **16**, 1690 (1951).

(16) Ullmann and von Wursteinberger, *Ber.*, **38**, 4107 (1905).

(17) Schultz and Smullin, *J. Am. Chem. Soc.*, **62**, 2904 (1940).

(18) Greenhow, White, and McNeil, *J. Chem. Soc.*, 2848 (1951).

28–30°. This compound previously has been reported only as a liquid.

Anal. Calc'd for $C_{17}H_{18}$: C, 91.80; H, 8.20. Found: C, 91.96; H, 8.59.

9-n-Butylidene fluorene picrate. The picrate formed yellow crystals from ethanol melting at 111.5°.

Anal. Calc'd for $C_{23}H_{19}N_3O_7$: C, 61.41; H, 4.26; N, 9.34. Found: C, 61.83; H, 4.49; N, 9.13.

Pyrolysis of 9-n-propylidene fluorene. 9-n-Propylidene fluorene (72.1 g.) was pyrolyzed by atmospheric distillation under nitrogen from a distilling flask attached to a condenser using a receiver which was connected to a Dry Ice-acetone trap and a 4-l. separatory funnel filled with water and inverted in a trough. The distillation required 15 minutes and gave 60 g. of distillate. The black tarry residue (8.9 g.) was dissolved in benzene and filtered. Removal of the solvent gave a red glass which resisted crystallization and gave no definite bands when chromatographed upon an alumina column.

The distillate upon fractional distillation at 1 mm. and fractional crystallization gave fluorene (7.7 g.), 9-methylfluorene (5.7 g.), a mixture of fluorene and 9-methylfluorene (6.6 g.), 9-n-propylfluorene (15.9 g.), and 9-n-propylidene fluorene (6.8 g.). The five intermediate fractions amounted to 12.8 g. and the residue weighed 2.5 g. Identification of the alkylfluorenes was accomplished either by oxidation with potassium permanganate to the corresponding 9-alkyl-9-fluorenol or by nitration to the 2,7-dinitro-9-alkylfluorene. Fractional crystallization of the 9-alkyl-9-fluorenols gave no indications for the presence of 9-ethylfluorene. The 9-n-propylidene fluorene was identified as the picrate.

The volatile gases trapped in the separatory funnel gave the following analysis using a Perkin Elmer mass spectrometer. The results are based on an air-free sample.

Compound	Mole-Percent
Butanes	0.06
Butenes	0.09
Propane	1.2
Propylene	9.0
Ethane	44.
Ethylene	18.0
Acetylene	0.1
Methane	23.00
Carbon dioxide	5.0

The liquid in the Dry Ice-acetone trap from qualitative tests and the wide boiling point range apparently consisted of olefins and saturated hydrocarbons with five or more carbon atoms.

The above procedure with the exception of the gas analyses was also used with 9-ethylidene fluorene and 9-n-butylidene fluorene.

Pyrolysis of 9-ethylidene fluorene. The pyrolysis of 9-ethylidene fluorene¹⁸ (192 g.) gave 124 g. of distillate which upon fractional distillation and crystallization gave fluorene (30.8 g.), 9-methylfluorene (29.2 g.), 9-ethylfluorene (12.5 g.), and 9-ethylidene fluorene (3.8 g.).

Pyrolysis of 9-n-butylidene fluorene. The pyrolysis of 9-n-butylidene fluorene¹⁹ (55 g.) gave 46.5 g. of a dark red distillate. Fractionation gave fluorene (3.1 g.), 9-methylfluorene (2.2 g.), a mixture of fluorene and 9-methylfluorene (3.4 g.), 9-n-butylfluorene (17.8 g.), and 9-n-butylidene fluorene (6.4 g.).

Acknowledgment. The authors wish to thank Dr. Fred McLafferty of the Dow Chemical Company for carrying out the analysis of the volatile gases.

(19) Sprinzak, *J. Am. Chem. Soc.*, **74**, 2116 (1952).