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CONDENSATION OF ALDEHYDES WITH FLUORENE AND NITROFLUORENES[1, 2]

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In a study of wetting agents of special structures derived from fluorene it became necessary to investigate the condensation of this hydrocarbon and some of its nitro derivatives with aldehydes. The reaction has been shown to lead to 9-alkylidene or 9-arylidene fluorenes in certain cases. Schultz and Smullin (8) condensed propionaldehyde, butyraldehyde, and isobutyraldehyde with fluorene successfully using potassium ethoxide as catalyst. We have followed their directions in obtaining the corresponding products from *n*-hexaldehyde and *n*-heptaldehyde. These alkylidene fluorenes were yellow, crystalline solids which decomposed slowly in air, forming an oil and generating an aldehyde odor. They were easily reduced at room temperatures with hydrogen in the presence of platinum oxide, but not with aluminum amalgam in moist ether (12), to the corresponding 9-alkylfluorenes (Table I).

Sulfonation of the 9-alkyl-fluorenes with concentrated sulfuric acid gave the 9-alkyl-2-fluorenesulfonic acids which were obtained as salts by neutralization of the acids with the appropriate bases. The solubilities and surface-tension-lowering effects of these salts in water were determined. The S-benzylisothiuronium salts were prepared for characterization and analysis (Table II). The position of the sulfonic acid group was established by oxidation to potassium 9-fluorenone-2-sulfonate (11) and conversion of this to its 9-oxime, a known compound (1). Sulfonation of 9-heptylfluorene with chlorosulfonic acid in carbon tetrachloride solution (6) at 12° gave the disulfonic acid chloride rather than the desired monosulfonic acid chloride.

The mononitration of fluorene is successfully accomplished in glacial acetic acid using concentrated nitric acid (7). Dinitrofluorenes may be prepared from fluorene with glacial acetic acid-fuming nitric acid nitrating mixture (5). The dinitration of 9-alkyl fluorenes, however, was found to require more vigorous conditions. Nitration was accomplished at 50° using a mixture of concentrated sulfuric acid and concentrated nitric acid as the nitrating agent. Low yields of the 2,7-dinitro-9-alkylfluorene were obtained (Table IV).

The condensation of 2,7-dinitrofluorene with aromatic aldehydes in the presence of piperidine at 160° is reported by Candea and Hobrescu (2), although the purity of their starting material is questionable. We have found that similar condensations with benzaldehyde, *p*-chlorobenzaldehyde, and *p*-propoxybenzaldehyde occur readily with 2,7- or 2,5-dinitrofluorene at less elevated temperatures. Benzaldehyde reacts even at room temperature, the others in refluxing xylene. Piperidine is a suitable catalyst.

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TABLE I

9-ALKYL AND 9-ALKYLIDENE FLUORENES

NAME	YIELD, %	M.P. OR B.P.	n_D^{20}	d_4^{25}	FORMULA	ANAL., C, H			
						Calc'd		Found	
9-Butylfluorene	73	145 (5 mm.)	1.5950	1.037	$C_{17}H_{18}$	91.84	8.11	92.15	7.92
9-Hexylidenefluorene	45.7	44–45			$C_{19}H_{20}$	91.88	8.12	91.95	8.10
9-Hexylfluorene	76	165 (3 mm.)	1.5778	1.054	$C_{19}H_{22}$	91.14	8.86	91.23	9.06
9-Heptylidenefluorene	57.4	56–58			$C_{20}H_{22}$	91.54	8.45	91.0	9.02
9-Heptylfluorene	75	172 (1 mm.)	1.5689	1.017	$C_{20}H_{24}$	90.84	9.15	90.6	9.18

TABLE II

SALTS OF 9-ALKYL-2-FLUORENESULFONATES

SALT	YIELD, %	M.P., °C.	WATER SOLUBILITY, G./ML.	SURFACE TENSION, DYNES/CM.	FORMULA	ANAL., N	
						Calc'd	Found
9-Butyl-2-fluorenesulfonates							
Ammonium	42	175–178	0.778	56.4[a]			
S-Benzylisothiuronium		149–150			$C_{25}H_{28}N_2O_3S_2$	5.98	6.02
9-Hexyl-2-fluorenesulfonates							
Sodium	74	318–319	0.307	60.6[a]			
S-Benzylisothiuronium		145–146			$C_{27}H_{32}N_2O_3S_2$	5.64	5.63
9-Heptyl-2-fluorenesulfonates							
Potassium	41.5	294	0.136	50.6[a]			
S-Benzylisothiuronium		127–128			$C_{28}H_{34}N_2O_3S_2$	5.49	5.46
Ethanolammonium				48.4[b]			

[a] Saturated aqueous solution.

[b] A 5.6% solution. Solubility not determined.

TABLE III

CONDENSATION PRODUCTS OF NITROFLUORENES WITH ALDEHYDES

NAME	YIELD, %	M.P.	FORMULA	ANAL., N	
				Calc'd	Found
2,7-Dinitro-9-heptylidenefluorene	45.5	216–217°	$C_{20}H_{20}O_4N_2$	7.95	7.89
2,7-Dinitro-9-hexylidenefluorene	49	254–255°	$C_{19}H_{18}O_4N_2$	8.28	8.44
2,5-Dinitro-9-heptylidenefluorene	29	163–164°	$C_{20}H_{20}O_4N_2$	7.95	7.69
1,1-Bis-(2′,7′-dinitrofluorenyl)butane	73	255°	$C_{30}H_{25}O_8N_4$	9.83	10.12
1,1-Bis-(2′-nitrofluorenyl)heptane	34.2	219–220°	$C_{33}H_{30}O_4N_2$	5.40	5.32
2,7-Dinitro-9-benzylidenefluorene	36	235–236°	$C_{20}H_{12}O_4N_2$	8.14	8.09
2,7-Dinitro-9-*p*-chlorobenzylidenefluorene	42.4	268–269°	$C_{20}H_{11}O_4N_2Cl$	7.40	7.37
2,7-Dinitro-9-*p*-propoxybenzylidenefluorene	28.5	288–289°	$C_{23}H_{18}O_5N_2$	6.96	7.04
2,5-Dinitro-9-benzylidenefluorene	43	205–207°	$C_{20}H_{12}O_4N_2$	8.14	8.13

The reaction of dinitrofluorenes with aliphatic aldehydes has not been reported. Our attempts to effect the condensation with heptaldehyde using either alkali ethoxides, pyridine, or barium hydroxide as catalysts were unsuccessful. It was found however, that piperidine as catalyst gave the desired result.

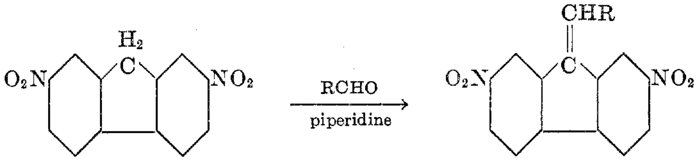
TABLE IV

SUBSTITUTED 9-ALKYLFLUORENES

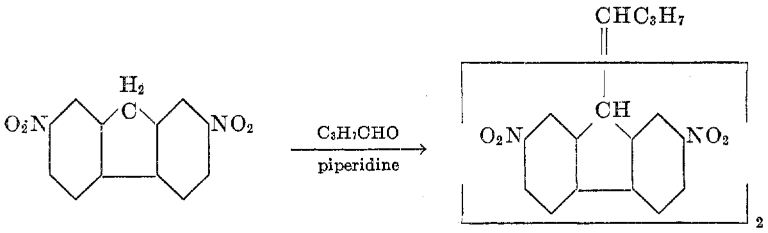
NAME	YIELD, %	M.P.	FORMULA	ANAL., N	
				Calc'd	Found
2,7-Dinitro-9-butylfluorene	8.6	163–164	$C_{17}H_{16}C_4N_2$	8.97	8.95
2,7-Dinitro-9-heptylfluorene	11	114–115°	$C_{20}H_{22}C_4N_2$	7.91	7.92
9-Heptyl-2,7-fluorenediamine[a]	90	255°	$C_{20}H_{28}N_2Cl_2$	7.63	7.46
9-Hexyl-2,7-fluorenediamine[b]	76	212–215°	$C_{33}H_{32}O_2N_2$	5.74	5.74
9-Benzyl-2,7-fluorenediamine	85	163–164°	$C_{20}H_{18}N_2$	9.80	9.75
9-Benzyl-2,5-fluorenediamine	77	166–167°	$C_{20}H_{18}N_2$	9.80	9.77
9-Heptyl-2,5-fluorenediamine	92	131–132	$C_{20}H_{26}N_2$	9.51	9.85

[a] Obtained as crude oil, characterized and analyzed as hydrochloride.

[b] Obtained as crude oil, characterized and analyzed as N,N'-dibenzoyl derivative (10).



Heptaldehyde was condensed by adding a dilute solution of the aldehyde dropwise to a refluxing mixture of 2,7-dinitrofluorene, piperidine and alcohol. Hexaldehyde was condensed by refluxing with 2,7-dinitrofluorene, piperidine and xylene for several hours (Table III). The same procedure with butyraldehyde gave only 1,1-bis-(2',7'-dinitrofluorenyl)butane rather than 2,7-dinitro-9-butylidenefluorene.



The yield of the bis product was increased by adding a dilute solution of the aldehyde dropwise to a rapidly refluxing mixture of 2,7-dinitrofluorene. This increase in yield may be explained in terms of the difference in the ratio of reactants available in the two experiments. In the second procedure the reaction occurs in the alcohol phase between a large excess of 2,7-dinitrofluorene and a limited amount of aldehyde. This favors the reaction of two molecules of 2,7-dinitrofluorene with one of the aldehyde. In the first procedure the reaction takes place in the alcohol phase containing a high concentration of aldehyde and a concentration of 2,7-dinitrofluorene limited by its solubility in xylene at the temperature used. The conditions are therefore not as favorable for the formation of the bis product, and hence the yield of this material is lowered. We were not successful in obtaining 2,7-dinitro-9-butylidenefluorene.

The formation of bis products also occurs in the hitherto unstudied condensation of aldehydes with 2-nitrofluorene. The sodium salt (4) of the latter reacts with heptaldehyde to give poor yields of 1,1-bis-(2′-nitrofluorenyl)heptane. The use of piperidine (3) as catalyst, or no catalyst at all, gave the same product from 2-nitrofluorene and heptaldehyde. These products are shown in Table III.

Catalytic reduction of the various alkylidene nitrofluorenes gave the corresponding alkylfluorene amines in good yields (Table IV).

The most striking feature of the above described studies is the remarkable sensitivity of the condensations to change in conditions and reagents. Fluorene and its nitration products behave quite differently towards the same aldehyde, and different aldehydes behave quite differently towards any one of the fluorene compounds. In general, a careful study of catalysts, solvents, and reaction times and temperatures is necessary to obtain satisfactory yields of the desired 9-alkylidene fluorenes. The details described in the experimental part represent the best, or in some cases the only, conditions found satisfactory for the indicated products. Condensations involving aliphatic aldehydes are more difficult to control than those involving aromatic aldehydes, probably because of the tendency of the former to condense with themselves and form dimers or polymers. Nitro groups in the 2-,5-, and 7-positions or combinations of these on the fluorene nucleus make the reaction even more sensitive to conditions than with fluorene itself. No suitable method for condensing 2-nitrofluorene with an aliphatic aldehyde in a 1:1 ratio was found. Likewise no success attended several efforts to condense chloral with 2-nitrofluorene or 2,7-dinitrofluorene using various catalysts and reaction conditions. This is surprising in view of the ready reaction of this aldehyde with other active methyl and methylene groups.

The salts of the 9-alkylfluorene-2-sulfonates show a rather low order of water solubility and surface activity compared to similar compounds in the naphthalene series. Their suitability as wetting agents is therefore questionable. Likewise the quaternary ammonium salt, N,N,N-trimethyl-9-benzyl-2-fluorenammonium acid sulfate, was so insoluble and inactive that saturated aqueous solutions of it did not froth when shaken vigorously.

EXPERIMENTAL

Generally only one representative example of each reaction procedure is described. Yields, physical properties and analytical data are given in Tables I–IV. The microanalyses were done by Dr. H. Galbraith of Purdue University.

9-Heptylidenefluorene. Absolute alcohol (20 cc.) was slowly added to a solution of potassium (7.8 g.) in xylene (300 cc.) under a nitrogen atmosphere. Fluorene (33 g.) was added after the reaction subsided. The rapidly-stirred mixture was heated to boiling and then allowed to cool to room temperature. Heptaldehyde (27.4 g.) in xylene (100 cc.) was slowly added dropwise. The mixture was heated to boiling after the addition of aldehyde was completed. After the solution returned to room temperature, hydrochloric acid was added to neutrality. The solvent and unreacted aldehyde were then removed by steam distillation. The viscous oily residue was separated from the aqueous layer by decantation and allowed to remain in an ice-bath over-night. The solid obtained was recrystallized to give 9-heptylidenefluorene, 30.5 g., (57.4%). Three recrystallizations from alcohol gave a yellow solid, m.p. 56–58°.

Anal. Calc'd for $C_{20}H_{22}$: C, 91.5; H, 8.5.
Found: C, 91.0; H, 9.02.

9-Heptylfluorene. A solution of 9-heptylidenefluorene (23.6 g.) in absolute alcohol (100 cc.) was shaken with hydrogen in the presence of platinum oxide at room temperature and an initial pressure of 60 p.s.i. The reduction was completed within 8 hours. After filtration of the catalyst the solvent was removed by evaporation. The viscous, oily residue was distilled under reduced pressure to give 9-heptylfluorene, 17.5 g. (75%), b.p. 172° (1 mm.), n_D^{20} 1.5689, d_4^{25} 1.017.

Anal. Calc'd for $C_{20}H_{24}$: C, 90.9; H, 9.10.
Found: C, 90.6; H, 9.18.

Sulfonation of 9-heptylfluorene with chlorosulfonic acid. To a solution of 9-heptylfluorene (9.3 g.) in carbon tetrachloride (80 cc.), chlorosulfonic acid (8 g.) was added dropwise with good stirring during 2.5 hours. The temperature was maintained at 12° and the reaction was allowed to proceed for 4 more hours at 12°. The carbon tetrachloride layer was decanted onto ice, leaving behind a tarry residue. The latter was washed with ether and the ether washings combined with the carbon tetrachloride layer. The residue was taken up in distilled water and neutralized with solid potassium carbonate. The solution was evaporated to dryness and extracted with alcohol in a Soxhlet for 48 hours; dipotassium 9-heptylfluorenedisulfonate (1.5 g.) was obtained as crystals in the extraction flask. Two recrystallizations from an ethanol-water solution produced a crystalline material, which decomposed over a range above 290°.

Anal. Calc'd for $C_{20}H_{22}K_2O_6S_2$: K, 15.6. Found: K, 16.3.

The combined carbon tetrachloride and ether solutions were washed with water and dried. The solvents were evaporated leaving a tarry material (10 g.). The residue was crystallized from petroleum ether (60–70°) to give 9-heptylfluorenedisulfonyl chloride. Two crystallizations from petroleum ether gave a white crystalline solid, m.p. 113°.

Anal. Calc'd for $C_{20}H_{22}Cl_2O_4S_2$: C, 51.9; H, 4.74.
Found: C, 52.0; H, 4.74.

Potassium 9-heptyl-2-fluorenesulfonate. 9-Heptylfluorene (16.6 g.) and excess concentrated sulfuric acid were rapidly stirred together for 12 hours at 45°. The temperature was raised to 100° and the stirring continued for 12 hours. The acid layer was removed by decantation, and the black viscous residue was dissolved in water. The aqueous solution was basified with potassium carbonate, which precipitated a white solid. Crystallization from 50:50 ethanol-water gave 6.2 g. (41.5%) of white, crystalline potassium 9-heptyl-2-fluorenesulfonate, m.p. 294°.

S-Benzylisothiuronium 9-heptyl-2-fluorenesulfonate. A saturated aqueous solution of S-benzylisothiuronium chloride (0.25 g.) was added to a solution of potassium 9-heptyl-2-fluorenesulfonate (0.25 g.) dissolved in the minimum amount of boiling water. The precipitate was recrystallized several times from a 50:50 ethanol-water solution. Acidification with hydrochloric acid gave a white crystalline solid, m.p. 127–128°.

Anal. Calc'd for $C_{28}H_{34}N_2O_3S_2$: N, 5.53. Found: N, 5.46.

Nitration of 9-heptylfluorene. Concentrated nitric acid (4 cc.) was added in 5 minutes to a rapidly stirred mixture of 9-heptylfluorene (5 g.) and sulfuric acid (4 cc.) maintained at 12°. The temperature was raised to 100° and the mixture was stirred for 15 minutes longer, and poured onto ice. The aqueous layer was removed by decantation and the viscuous, oily residue dissolved in ether. The ether solution was washed with bicarbonate and water. After the ether was removed, the residue was dissolved in ethanol at room temperature and allowed to crystallize overnight in an ice-bath to obtain 2,7-dinitro-9-heptylfluorene, 0.5 g. (11%). Two recrystallizations from glacial acetic acid gave a yellow crystalline solid, m.p. 114–115°.

Anal. Calc'd for $C_{20}H_{22}N_2O_4$: N, 7.89. Found: N, 7.92.

2,7-Dinitro-9-benzylidenefluorene. A mixture of benzaldehyde (15 g.), 2,7-dinitrofluorene (15 g.), piperidine (20 drops) and alcohol (100 cc.) was rapidly stirred at room temperature for 24 hours. The mixture was filtered, and the solid crystallized from glacial acetic acid to give 2,7-dinitro-9-benzylidenefluorene, 8 g. (36%). Two recrystallizations from glacial acetic acid gave a yellow solid, m.p. 235–236°.

Anal. Calc'd for $C_{20}H_{12}N_2O_4$: N, 8.14. Found: N, 8.09.

2,5-Dinitro-9-benzylidenefluorene. A mixture of benzaldehyde (12 g.), 2,5-dinitrofluorene (30 g.), piperidine (50 drops) and alcohol (240 cc.) was refluxed for 2 hours, cooled and filtered. The solid was crystallized from glacial acetic acid to give 2,5-dinitro-9-benzylidenefluorene (20 g., 43% yield). Two crystallizations from glacial acetic acid gave a yellow solid, m.p. 205–207°.

Anal. Calc'd for $C_{20}H_{12}N_2O_4$: N, 8.14. Found: N, 8.13.

2,7-Dinitro-9-p-propoxybenzylidenefluorene. A mixture of 2,7-dinitrofluorene (15 g.), *p*-propoxybenzaldehyde (12 g.), piperidine (30 drops) and xylene (210 cc.) was refluxed for 2 hours and filtered hot. The residue (2 g.), m.p. 292° dec., was unreacted 2,7-dinitrofluorene. The mother liquor was concentrated, cooled, and filtered. The yellow solid was crystallized from xylene to give 2,7-dinitro-9-*p*-propoxybenzylidenefluorene, 6.7 g. (28.5%). Three recrystallizations from xylene gave a yellow crystalline solid, m.p. 288–289°.

Anal. Calc'd for $C_{23}H_{19}N_2O_5$: N, 6.98. Found: N, 7.04.

2,7-Dinitro-9-heptylidenefluorene. A solution of heptaldehyde (21 g.) in absolute alcohol (500 cc.) was slowly added (12 hours) to a rapidly refluxing mixture of 2,7-dinitrofluorene (45 g.), piperidine (6 cc.) and absolute alcohol (150 cc.). The cooled mixture was filtered and the solid crystallized from glacial acetic acid to give 2,7-dinitro-9-heptylidenefluorene, 30 g. (45.5%). Three recrystallizations from glacial acetic acid gave a pale yellow solid, m.p. 216–217°.

Anal. Calc'd for $C_{20}H_{26}N_2O_4$: N, 7.92. Found: N, 7.89.

2,7-Dinitro-9-hexylidenefluorene. A mixture of hexaldehyde (3 g.), 2,7-dinitrofluorene (5 g.), piperidine (10 drops) and xylene (70 cc.) was refluxed for 2 hours and filtered hot. The residue was unreacted 2,7-dinitrofluorene (0.5 g.), m.p. 288–289° (dec.). Concentration of the solution and cooling produced 2,7-dinitro-9-hexylidenefluorene, 3.4 g. (49%). Two crystallizations from xylene gave a yellow crystalline material, m.p. 254–255°.

Anal. Calc'd for $C_{19}H_{18}N_2O_4$: N, 8.29. Found: N, 8.44.

1,1-Bis-(2′,7′-dinitrofluorenyl)butane. (a) A solution of butyraldehyde (3 g.) in absolute alcohol (100 cc.) was added dropwise in 1 hour to a rapidly refluxing mixture of 2,7-dinitrofluorene (5 g.), piperidine (10 drops) and absolute alcohol (50 cc.). The cooled mixture was filtered and the solid crystallized from xylene to give 1,1-bis-(2′,7′-dinitrofluorenyl)-butane, 4.3 g. (73.3%), m.p. 255°.

(b) A mixture of butyraldehyde (3 g.), 2,7-dinitrofluorene (15 g.), piperidine (30 drops) and xylene (210 cc.) was refluxed for one hour and filtered hot. On cooling, the filtrate precipitated 1,1-bis-(2′,7′-dinitrofluorenyl)butane, 3.5 g. (24%). Three crystallizations from xylene gave a pale yellow solid, m.p. 254–255°.

Anal. Calc'd for $C_{30}H_{18}N_4O_8$: N, 9.99. Found: N, 10.12.

1,1-Bis-(2′-nitrofluorenyl)heptane. A mixture of 2-nitrofluorene (5 g.), *n*-heptaldehyde (5.2 g.) and hexanol (25 cc.) was refluxed for 12 hours. On cooling 1,1-bis-(2′-nitrofluorenyl)-heptane, 0.9 g., (15%) crystallized from the solution. Four recrystallizations from glacial acetic acid gave a yellow crystalline solid, m.p. 219–220°.

Anal. Calc'd for $C_{33}H_{30}N_2O_4$: N, 5.40. Found: N, 5.32.

9-Heptyl-2,5-fluorenediamine. A slurry of 2,5-dinitro-9-heptylidenefluorene (4.2 g.) and absolute alcohol (75 cc.) was shaken with hydrogen and platinum oxide at room temperature and an initial pressure of 60 p.s.i. The reduction was completed within 8 hours. Concentration of the solution yielded a yellow crystalline solid which was recrystallized from alcohol to give 9-heptyl-2,5-fluorenediamine, 3.2 g. (92%). Two recrystallizations from alcohol gave a yellow crystalline solid, m.p. 131–132°.

Anal. Calc'd for $C_{20}H_{26}N_2$: N, 9.55. Found: N, 9.85.

9-Benzyl-2-fluoreneamine. A slurry of 2-nitro-9-benzylidenefluorene (36 g.) (5) and absolute alcohol (500 cc.) was shaken with hydrogen and Raney nickel at 130° at an initial pressure of 1000 p.s.i. The reduction was completed within 24 hours. The oily product (26.4 g., 86.5% crude yield) was not further purified, but was immediately methylated as described below.

N,N,N-Trimethyl-9-benzyl-2-fluorenammonium acid sulfate. To a portion of the crude amine (4.4 g.) and ether (50 cc.), methyl sulfate (2.0 g.) was slowly added under reflux. After the addition was completed the solution was cooled and basified with 20% sodium hydroxide. The aqueous layer was removed by decantation and the first operation was repeated using another portion of methyl sulfate (8 g.). The aqueous solution was neutralized with 20% sodium hydroxide and washed with ether. A white solid precipitated from the aqueous layer. The solid was crystallized from a water-alcohol solution to give N,N,N-trimethyl-9-benzyl-2-fluorenammonium acid sulfate. Two recrystallizations from alcohol-water solution gave a white crystalline solid, m.p. 185°.

Anal. Calc'd for $C_{23}H_{22}NO_4S$: N, 3.43. Found: N, 3.45.

SUMMARY

A study has been made of the condensations of aliphatic and aromatic aldehydes with fluorene and nitrofluorenes. The resulting products have been reduced to 9-alkylfluorenes and 9-alkylfluoreneamines. The 9-alkyfluorenes have been sulfonated and then neutralized to obtain surface-active compounds of new types.

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