170–190° (bath temperature). The cooled mixture was poured on ice, diluted, and neutralized with excess barium carbonate. After digestion, filtration, and evaporation of the filtrate to dryness 144 g. (93%) of barium 4-ethyl-3,5-disulfobenzoate was obtained; *p-toluidine salt*[9]: m.p. 287–289° dec. (297–299° corr.).

Anal. Calcd. for $C_{23}H_{28}O_8N_2S_2$: C, 52.5; H, 5.34; N, 5.34; neut. equiv., 174.9. Found: C, 52.2; H, 5.48; N, 5.22; neut. equiv.,[10] 174.6.

The *sulfonyl chloride* was obtained as white rods (from ligroin), m.p. 82–83°.

Anal. Calcd. for $C_9H_7O_5S_2Cl_3$: S, 17.54. Found: S, 17.38.

The *sulfonamide* was obtained as white crystals (from water), m.p. 269° dec. (rate of heating 1°/min.).

Anal. Calcd. for $C_9H_{13}O_6S_2N_3$: S, 20.87. Found: S, 20.97.

3,5-Disulfoterephthalic acid. A mixture of 5.00 g. (0.00187 mole) of barium 4-ethyl-3,5-disulfobenzoate and 30 ml. of fuming nitric acid (*d*, 1.5 g./ml.) was heated in a sealed tube (enclosed in an iron pipe) for 6.5 hr. at 170–184° (183–196° bath temperature). After evaporating excess nitric acid, 100 ml. of water was added with stirring. Barium sulfate was filtered off and the filtrate was neutralized by the addition of 2.3 g. of barium carbonate. The white, flocculent precipitate which formed in the hot solution was removed (2.3 g.) and was recrystallized from dilute hydrochloric acid, yielding glistening, translucent needles.

Anal. Calcd. for $C_{16}H_6O_{20}S_4Ba_3$: Ba, 38.9. Found: Ba, 38.4.

p-Toluidine barium salt[9]:

Anal. Calcd. for $C_{30}H_{24}O_{20}S_4N_2Ba_3$: S, 10.1; neut. equiv., 636. Found: S, 10.2; neut. equiv.,[10] 641.

Alkali fusion. Barium 4-ethyl-3,5-disulfobenzoate (167 g.) was stirred into 516 g. of molten potassium hydroxide in a large copper beaker, and the mixture was kept at 260–290° for 2 hr. The melt was then poured into water, barium sulfite was filtered, and the filtrate was acidified with excess concentrated hydrochloric acid. The resulting brown precipitate (10 g., mainly hydroxyterephthalic acid and 4-ethyl-3-hydroxybenzoic acid) was filtered and the filtrate was extracted with ether, yielding 36.7 g. of a tan solid.

Hydroxyterephthalic acid. The brown solid (10 g.) obtained on acidification of the melt was boiled with 100 ml. of water. The mixture was filtered, and the residue was recrystallized twice from aqueous methanol, yielding a white substance melting between 312° and 327° (with sublimation) depending on the rate of heating (reported[11] m.p. 327°).

Anal. Calcd. for $C_8H_6O_5$: Neut. equiv., 91.1. Found: Neut. equiv., 91.7.

Dinitroderivative: m.p. 177–178° (reported[12] 178°).

Chromatography. The tan solid (36.7 g.) obtained from the ether extraction of the acidified melt was stirred with 367 ml. of water at 55° for 5 min., and the mixture was filtered. The filtrate was treated with 106 g. of salt, the resulting precipitate was filtered, and the filtrate was extracted with ether. A 6.5-g. portion of the material obtained by evaporation of the ether was dissolved in 30 ml. of hot water, mixed thoroughly with 75 g. of silicic acid, and covered with hexane. This mixture was ladled into a 92 cm. high (8 cm. I.D.) column packed with 1.6 kg. of silicic acid (100 mesh, containing 28.6% water) to a height of 65 cm., and covered with hexane. Elution was effected with mixtures of butanol in hexane, the percent of butanol (by volume) rising gradually from 1% to 4.5%. Fifteen-milliliter samples were collected at an average flow rate of 1.5 ml./min. One-milliliter aliquots were titrated against 0.0025*N* alcoholic potassium hydroxide.

4-Ethyl-3-hydroxybenzoic acid. The first fraction obtained from the chromatography contained 0.46 g. of a substance, which after recrystallization from water melted at 169° and did not depress the melting point of an authentic specimen of 4-ethyl-3-hydroxybenzoic acid.[13]

3-Hydroxy-4-methylbenzoic acid (II). The second fraction obtained from the chromatography followed immediately after the separation of the first one, and contained 0.90 g. of a substance which crystallized from water in needles, m.p. 206–207° (reported[14] 206–207°), and which did not depress the melting point of an authentic specimen.

Anal. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30; neut. equiv., 152. Found: C, 63.00; H, 5.30[15]; neut. equiv., 155.

m-Hydroxybenzoic acid. The third fraction obtained from the chromatography did not appear until long (137 fractions) after the second one had separated, and contained 2.24 g. of a substance which melted at 199–200°, and did not lower the melting point of an authentic specimen of *m*-hydroxybenzoic acid.

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Derivatives of Fluorene. XIII. Formation of 9-Arylimino Compounds in the Presence of Boron Trifluoride

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Received June 27, 1960

In previous papers[3] we reported use of several catalysts in the formation of 9-aryliminofluorenes. In a search for catalysts which, while highly effective, can be used under milder conditions, we have found that boron trifluoride, used as the diethyl etherate, effects condensation at lower temperatures than are necessary with zinc chloride and others.

Twenty-four azomethine derivatives of fluorene, mostly new, have been prepared in excellent yield, either in a suitable solvent or by fusion. The latter was resorted to when the substituted fluorenone was relatively insoluble. In Table I a few boron trifluoride catalyzed condensations are compared with fusions of the same starting materials in the presence of zinc chloride.

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(2) This work was supported in part by a research grant (C-1744) from the National Cancer Institute of the National Institutes of Health, Public Health Service.

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TABLE I

COMPARISON OF BORON TRIFLUORIDE AND ZINC CHLORIDE AS CATALYSTS IN THE FORMATION OF AZOMETHINES

Compound	Catalyst	Time, min.	Temp.	Solvent[a]	Yield, %
N-(2,5-Dinitrofluorenylidene)-*p*-toluidine	BF_3	10	125–130	—	90
	$ZnCl_2$	45	165–175	—	92
N-(2-Nitrofluorenylidene)-*p*-toluidine	BF_3	10	120–125	—	100
	$ZnCl_2$	45	160–170	—	72
N-(2,4,7-Trinitrofluorenylidene)-*p*-toluidine	BF_3	60	Reflux	Benzene	40
	BF_3	120	Reflux	Benzene	100
	$ZnCl_2$	30	165–170	—	72
N-Fluorenylidene-*p*-fluoroaniline	BF_3	19 (hr.)	25–30	Chloroform	100[b]
	BF_3	48 (hr.)	25–30	Chloroform	100[c]
	BF_3	30	120–125	—	93
	$ZnCl_2$	60	170–175	—	87

[a] — indicates a fusion reaction. [b] 64% from initial filtration and an additional 34% by boiling down the chloroform. [c] 78% from initial filtration and 22% (see [b]).

In the solution method a small amount of absolute ethanol was usually added to solubilize the boron trifluoride–amine compound. After refluxing the reaction mixture the alcohol was boiled away, precipitating the addition compound which was removed by filtration. Further concentration led to recovery of the azomethine. In condensations with *m*-toluidine, the addition product with boron trifluoride was soluble in the solvents used and was recovered with the azomethine. Purification in these cases was accomplished by triturating the product with absolute ethanol, filtration, and washing with the same solvent. Recrystallization before removal of the amine complex gave a deteriorated product.

p-Chloroaniline and 2,4,7-trinitrofluorenone were allowed to stand for three days in chloroform with boron trifluoride etherate. A purple addition compound resulted which melted at 146–147°. Upon heating below 145° for a short while the substance lost weight, becoming colorless. The residue was 2,4,7-trinitrofluorenone. When the purple substance was refluxed in chloroform with boron fluoride, and a little alcohol added, the azomethine was obtained as red needles.

Tables II summarizes the experimental data.

EXPERIMENTAL[4]

Typical procedures used in preparing azomethines in the presence of boron trifluoride by fusion, in solution at room temperature and in refluxing solvents are illustrated by specific examples.

Preparation of N-fluorenylidene-p-chloroaniline in refluxing chloroform. A solution of 9.0 g. (0.05 mole) of fluorenone, 10.2 g. (0.08 mole) of *p*-chloroaniline and 1 ml. of boron fluoride etherate in 100 ml. of chloroform with a few ml. of ethanol was refluxed for 15 min. The solution was concentrated to about 25 ml., yielding 14.5 g. (100%) of product, m.p. 145–148°. Recrystallization from chloroform-ethanol (1:3) gave yellow needles, m.p. 149.5–150.0°.

Preparation of N-(2,5-dinitrofluorenylidene)-p-toluidine by fusion. A mixture of 5.4 g. (0.02 mole) of 2,5-dinitrofluorenone (m.p. 243.5–244.5°), 4.3 g. (0.04 mole) of *p*-toluidine and 1 ml. of boron trifluoride etherate was fused at 125–130° for 10 min. with manual stirring. The product was dissolved in hot chloroform and filtered. The filtrate was concentrated to 50 ml. and 6.5 g. (90%) of red product crystallized, m.p. 201–203°. Recrystallization from acetone raised the m.p. to 202–203°.

Preparation of N-fluorenylidene-p-fluoroaniline at room temperature in chloroform. Boron trifluoride etherate (1.5 ml.) was added to a solution of 9.0 g. (0.05 mole) of fluorenone and 8.9 g. (0.08 mole) of freshly distilled *p*-fluoraniline in 10 ml. of chloroform at room temperature. The contents of the flask solidified. The solid was partially dissolved by adding 4 ml. of absolute ethanol and mixing. The flask was then stoppered and allowed to stand for 19 hr. A few milliliters of ethanol were then added and the product was collected by filtration and washed with ethanol yielding 8.8 g. (64%), m.p. 139–142°. Concentration of the filtrate to 20 ml. gave another 4.9 g. (36%) of product, m.p. 138–141°.

Preparation of the p-chloroaniline-2,4,7-trinitrofluorenone addition compound. A mixture of 7.9 g. (0.025 mole) of 2,4,7-trinitrofluorenone (m.p. 173.5–174.5°), 5.1 g. (0.04 mole) of *p*-chloroaniline and 0.5 ml. of boron trifluoride etherate in 50 ml. of chloroform and 3 ml. of absolute ethanol stood at room temperature for 3 days. The mixture was then filtered and washed with absolute ethanol, yielding 10.7 g., m.p. 138–144° (taken rapidly). Recrystallization from chloroform-ethanol raised the m.p. to 146–147°.

Anal. Calcd. for $C_{19}H_{14}ClN_4O_8$: C, 52.02; H, 2.50; Cl, 8.08; N, 12.77. Found: C, 51.82; H, 2.43; Cl, 8.17; N, 12.53.

When this compound was heated for a short time below 145°, it became colorless, m.p. 171–173° (mixture m.p. with authentic 2,4,7-trinitrofluorenone 171–173°).

Preparation of N-(2,4,7-trinitrofluorenylidene-p-chloroaniline from the addition compound. A solution of 9.4 g. of the addition compound in a minimum of hot chloroform with 4 ml. of absolute ethanol and 1 ml. of boron trifluoride etherate was refluxed for 7 hr. and cooled. A red product precipitated and was collected by filtration, 2 g., m.p. 217–220°. Crystallization from chloroform raised this m.p. to 231–231.5°.

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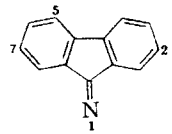
(4) All melting points are corrected. Melting points below 300° were taken on a Fisher-Johns block; over 300°, they were taken in a capillary in an aluminum block. Some microanalyses were done by Dr. W. Manser, Herrliberg (Zch), Switzerland; some by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and others by Drs. Weiler and Strauss, Oxford, England.

TABLE II. 9-ARYLIMINOLFLUORENE DERIVATIVES PREPARED WITH BF_3 AS A CATALYST[a]



No.	Ketone	Time, Min.	Temp.	M.P.	Yield, %	Crystal Color and Form	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
						FLUORENYLIDENE-*p*-TOLUIDINE COMPOUNDS								
1	Fluorenone (C)[b]	30	Reflux	119.5–120.0[c]	97	Yellow needles	89.18	88.89	5.61	5.66	5.20	5.10		
2	2-Nitrofluorenone	10	120–125	192–193[d]	100	Orange	76.42	76.22	4.49	4.31	8.91	8.83		
3	2,5-Dinitrofluorenone	10	125–130	202–203	90	Red					11.70	11.61		
4	2,7-Dinitrofluorenone	20	120–125	245.5–246	82	Red needles	66.85	66.73	3.65	3.64	11.70	11.66		
5	2,4,7-Trinitrofluorenone	120	Reflux	225.5–226	100	Maroon hairs					13.86	13.86		
6	2-Acetamidofluorenone	20	135–140	244–245	100	Yellow needles	80.95	80.65	5.56	5.52	8.58	8.38		
7	2-Benzamidofluorenone	45	120–125	228–228.5	91	Yellow	83.48	83.50	5.19	5.19	7.21	7.03		
						FLUORENYLIDENE-*m*-TOLUIDINE COMPOUNDS								
8	Fluorenone (C)	45	Reflux	101.5–102	87	Yellow needles	89.18	89.11	5.61	5.62	5.20	5.03		
9	2-Nitrofluorenone	20	120–125	188–189	100	Yellow needles	76.42	76.32	4.49	4.44	8.91	8.94		
10	2,5-Dinitrofluorenone	10	120–125	210–210.5	82	Orange hairs	66.85	66.73	3.65	3.69	11.70	11.66		
11	2,7-Dinitrofluorenone	15	115–125	233.5–234.5	97	Scarlet	66.85	66.76	3.65	3.66	11.70	11.69		
12	2,4,7-Trinitrofluorenone (B)	15	Reflux	182–183	67	Red	59.41	59.57	2.99	3.18	13.86	13.95		
13	2-Acetamidofluorenone	15	135–140	169–170	85	Yellow	80.95	80.95	5.56	5.61	8.58	8.74		
14	2-Benzamidofluorenone	60	125–130	188.5–189.5	37	Yellow	83.48	83.40	5.19	5.18	7.21	7.17		
						FLUORENYLIDENE-*p*-ANISIDINE COMPOUNDS								
15	Fluorenone (C)	30	Reflux	135–136[e]	100	Orange plates	84.18	83.98	5.30	5.08	4.91	5.05		
16	2-Nitrofluorenone	25	120–125	169–170	98	Orange plates	72.72	72.64	4.27	3.98	8.48	8.42		
17	2,5-Dinitrofluorenone	15	120–125	216.5–217.5	100	Maroon needles	64.00	64.05	3.49	3.62	11.20	11.10		
18	2,7-Dinitrofluorenone	20	Reflux	230.5–231.5	91	Red needles	64.00	63.97	3.49	3.61	11.20	11.05		
19	2,4,7-Trinitrofluorenone (B)	60	Reflux	230–231	97	Red hairs	57.15	57.23	2.88	2.95	13.33	13.32		
20	2-Acetamidofluorenone	30	135–140	227.5–228.5	85	Orange plates	77.17	76.74	5.30	5.10	8.18	7.90		
21	2-Benzamidofluorenone	30	125–130	227–229	100	Yellow					6.92	6.95		
						FLUORENYLIDENE-*p*-CHLOROANILINE COMPOUNDS								
22	Fluorenone (C)	15	Reflux	149.5–150[f]	100	Yellow needles	78.74	78.67	4.18	4.33	4.83	4.64	12.24	11.95
23	2-Nitrofluorenone (T)	120	Reflux	228–229	82	Orange hairs	68.16	68.26	3.31	3.48	8.37	8.39		
24	2,5-Dinitrofluorenone	15	125–130	234–235	100	Red needles	60.09	60.31	2.77	2.65	11.09	10.87		
25	2,7-Dinitrofluorenone	20	120–125	258–258.5	100	Orange needles	60.09	59.77	2.77	2.50	11.09	10.87	9.34	9.38
26	2,4,7-Trinitrofluorenone (T)	210	Reflux	231–231.5	72	Red needles	53.72	53.87	2.14	2.21	13.19	13.10	8.35	8.56
27	2-Acetamidofluorenone	30	115–120	228–229	95	Yellow needles	72.72	73.11	4.36	4.18	8.08	7.95		
28	2-Benzamidofluorenone	45	125–130	222.5–223.5	89	Yellow needles	76.38	75.86	4.19	4.20	6.85	6.95	8.67	9.13.

[a] Ketones were prepared as indicated in ref. 3. [b] B (benzene), C (chloroform), or T (toluene) indicates reaction solvent; absence of these letters indicates preparation by fusion. Ketones were prepared by methods listed. [c] Reported m.p. 122.5–123°, J. H. Billman and K. M. Tai, *J. Org. Chem.*, **23**, 536 (1958). [d] M. E. Taylor and T. L. Fletcher, *J. Am. Chem. Soc.*, **80**, 2246 (1958). [e] Reported[c] m.p. 135–136°. [f] Reported[c] m.p. 147–147.5°.

Products No. 7 and 16 were crystallized from acetonitrile, No. 8 from methanol, Nos. 9 and 24 from benzene, No. 12 from acetone, No. 13 from ethanol, No. 23 from chloroform-acetonitrile, and the rest from chloroform or chloroform-ethanol.