to the acid, IXA, in 80% yield by heating at 180–200° for two hours with potassium hydroxide in diethylene glycol. Crystallization from isopropyl ether afforded IXA, m.p. 97–100°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 82.1; H, 6.7.

Similarly the nitrile, VIIIB, was converted into IXB in 85% yield, the hydrolysis being effected by heating in diethylene glycol at 120–145° for two hours. Recrystallization of the crude acid from isopropyl ether afforded pure IXB, m.p. 151.4–152.2°.

Anal. Calcd. for $C_{18}H_{16}O_2$. C, 81.8; H, 6.1. Found. C, 81.8; H, 6.3.

4'-Keto-1'-methyl-1',2',3',4'-tetrahydro-1,2-benzanthracene, XA, and *4'-keto-1',2',3',4'-tetrahydro-1,2-benzanthracene*, XB. A mixture of 13.9 g. of crude acid, IXA, and 75 g. of polyphosphoric acid was heated at 80–110° for 45 min. The crude ketone, XA, m.p. 102–104°, was obtained in 80% yield. A pure sample, m.p. 105.0–106.5°, was obtained by chromatography over alumina and recrystallization from benzene and from isopropyl ether. A similar yield of crude ketone, XA, was obtained by cyclization of IXA with hydrogen fluoride.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.9; H, 6.3.

In a similar way, IXB was cyclized to the ketone, XB, in 85% yield, with hydrogen fluoride. Pure XB, m.p. 189.0–198.6°, was obtained by crystallization from benzene-isopropyl ether.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 88.0; H, 6.0.

1'-Methyl-1,2-benzanthracene, XIA, and *4'-methyl-1,2-benzanthracene*, XIB. After reduction of 2.6 g. of XA with lithium aluminum hydride in ether the crude alcohol was dehydrated by boiling with xylene to which a trace of iodine had been added. The crude dehydration product was treated with a slight excess of sulfur and heated at 220–240° for 10 min. A small amount of zinc dust was added and the heating continued for 10 min. at 200–220°. The product was taken up in benzene, filtered, chromatographed over alumina, treated with charcoal (Darco G-60) in acetone, and crystallized from acetone and from benzene to yield XIA, m.p. 137–138°, in 60% yield based on XA. Further purification along the same lines afforded XIA,[9] m.p. 139.2–139.9°.

A solution of 4.9 g. of XB in 200 ml. of tetrahydrofuran was added at 5–10° to the methyllithium prepared from 5.5 g. of lithium and 57 g. of methyl iodide[10] and the mixture was stirred for 30 min. After the usual workup the carbinol, m.p. 126–130°, was obtained in 85% yield. Without further purification the carbinol was dehydrated by boiling with xylene to which a trace of iodine had been added and the dehydration product was heated at 220–240° with a slight excess of sulfur for 10 min. Treatment with zinc dust and further treatment as above described for XIA afforded XIB, m.p. 190–192°, in 75% yield based on crude carbinol. Pure XIB,[11] 197.4–198.0°, was obtained after further crystallizations from acetone and benzene, and by chromatography over alumina.

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(9) For other syntheses of 1'-methyl-1,2-benzanthracene, see L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **60**, 170 (1938), J. W. Cook and A. M. Robinson, *J. Chem. Soc.*, 505 (1938), and W. E. Bachmann and R. O. Edgerton, *J. Am. Chem. Soc.*, **62**, 2550 (1940).

(10) K. Ziegler, *Ann.*, **479**, 135 (1930).

(11) For other syntheses of 4'-methyl-1,2-benzanthracene, see J. W. Cook, A. M. Robinson, and F. Goulden, *J. Chem. Soc.*, 505 (1938), C. Descamps and R. H. Martin, *Bull. soc. chim. Belges*, **61**, 223 (1952), B. M. Mikhailov and T. K. Kozminskaya, *Zhur. Obschei Khim.*, **23**, 1220 (1953); *Chem. Abstr.*, **47**, 12334 (1953); S. C. S. Gupta and D. N. Chatterjee, *J. Ind. Chem. Soc.*, **31**, 11 (1954).

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY OF THE DEPARTMENT OF SURGERY, UNIVERSITY OF WASHINGTON]

Derivatives of Fluorene. V. 9-Hydroxyfluorenes; Reduction of Fluorenones in the Presence of Aralkylideneamino Groups[1]

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Thirty-nine substituted 9-hydroxyfluorenes have been prepared and characterized. Sodium borohydride reduction of fluorenones is a convenient method for preparing many 9-fluorenols in good yields. Under certain conditions the —N=CH— group in some 2-aralkylideneaminofluorenones can be preserved while the carbonyl group is reduced. The reducibility of the —N=CH— group in 2-aralkylideneaminofluoren-9-ols can be made to vary by changing the type of para substituent in the aralkylidene group or by introducing a bromine in the 3-position of the fluorene moiety.

We have prepared[3] a number of substituted 9-hydroxyfluorenes by sodium borohydride reduction of the corresponding fluorenones,[4] and find that simplicity and high yields make this an excellent procedure (see Table I).

Upon being treated with sodium borohydride in our usual procedure, fluorenones with a ring —N=CHAr group gave mixtures including, in most instances, the corresponding benzylaminofluorenol compound. Billman and Diesing[5] recently reported

(1) This investigation was supported in part by a grant (C-1744) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

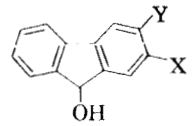
(2) To whom correspondence regarding this paper should be addressed.

(3) T. L. Fletcher and H. L. Pan, *J. Am. Chem. Soc.*, **78**, 4812 (1956).

(4) M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956). These authors reported the reduction of fluorenone with sodium borohydride in acetonitrile and methanol, obtaining 84% of the 9-ol after 6-hr. reflux of the complex in 20% aqueous potassium fluoride and dioxane.

(5) J. H. Billman and A. C. Diesing, *J. Org. Chem.*, **22**, 1068 (1957).

TABLE I. SUBSTITUTED 9-HYDROXYFLUORENES



X	Y	Ketone,[a,b] M.P., °C.	Yield, %	M.P.,[b] °C.	Empirical Formula	Analyses,[c] % Calcd. C	H	N	Br	Found C	H	N	Br
H	H	84.5–85	99	156–156.5 (Lit. m.p. 154–155°[d])									
NH_2	H	160–161	94	201–201.5 (Lit. m.p. 200°[e])									
CH_3NH-	H	159.5–160.5[g]	85	132–133	$C_{14}H_{13}NO$	79.59	6.20	6.63		79.59	6.29	6.54	
$(CH_3)_2N$	H	166–166.5[g]	100	159–159.5	$C_{15}H_{15}NO$	79.97	6.71	6.22		79.84	6.75	6.02	
C_2H_5NH	H	153–154.5[g]	94	146.5–147	$C_{15}H_{15}NO$	79.97	6.71	6.22		79.78	6.72	6.40	
$(C_2H_5)_2N$	H	101.5–102.5	90	135.5–136.5	$C_{17}H_{19}NO$	80.57	7.56	5.53		80.38	7.94	5.70	
n-C_3H_7NH	H	134–135	96	141–142	$C_{16}H_{17}NO$	80.30	7.16	5.85		80.30	7.32	6.00	
$(n$-$C_4H_9)_2N$	H	(Oil)	25[h]	111–112	$C_{21}H_{27}NO$	81.51	8.80	4.53		81.37	8.77	4.42	
n-C_4H_9NH	H	127.5–128.5	100	144–144.5	$C_{17}H_{19}NO$	80.57	7.56	5.53		80.85	7.57	5.58	
C_5H_9NH[i]	H	164–165	90	162–163	$C_{18}H_{19}NO$	81.47	7.22	5.28		81.55	7.20	5.43	
$C_6H_5CH_2NH$	H	149.5–150.5	100	159.5–160.5	$C_{20}H_{17}NO$	83.59	5.96	4.88		83.61	6.20	4.71	
$(C_6H_5CH_2)_2N$	H	139–140	97	150–151	$C_{27}H_{23}NO$	85.91	6.14	3.71		85.79	5.96	3.60	
$(p$-$BrC_6H_4CH_2)_2N$[j]	H	186–187	100	152–153	$C_{27}H_{21}Br_2NO$	60.58	3.96	2.62	29.86	60.64	3.98	2.64	29.71
p-$NO_2C_6H_4CH_2NH$	H	206–207	94	169.5–170.5	$C_{20}H_{16}N_2O_3$	72.28	4.85	8.43		72.21	4.78	8.52	
$(p$-$NO_2C_6H_4CH_2)_2N$[k]	H	212–213	92	177.5–178.5	$C_{27}H_{21}N_3O_5$	69.37	4.53	8.99		69.63	4.31	9.21	
p-Tosyl-NH	H	193.5–194.5[g]	78	218.5–219.5	$C_{20}H_{17}NO_3S$	68.35	4.88	3.99		68.05	4.50	3.99	
CH_3CONH	H	235–235.5	100	248.5–249.5[l]									
CH_3CONCH_3	H	157.5–159[g]	55	130.5–131.5	$C_{16}H_{15}NO_2$	75.87	5.97	5.53		76.11	6.00	5.38	
$CH_3CONC_2H_5$	H	138.5–139.5	100	141.5–142.5	$C_{17}H_{17}NO_2$	76.38	6.41	5.24		76.31	6.48	5.47	
CF_3CONH	H	249.5–250.5[m]	67	211.5–212.5	$C_{15}H_{10}F_3NO_2$	61.44	3.44	4.78		61.36	3.55	4.80	
$C_2H_5OOCCH_2NH$	H	146.5–147.5	100	130.5–131.5	$C_{17}H_{17}NO_3$	72.06	6.05	4.94		72.21	6.13	5.08	
$HOOCCH{=}CHCONH$[n]	H	225–230 (dec.)	100	>280	$C_{17}H_{13}NO_4$	69.14	4.44	4.74		69.35	4.54	4.75	
$C_6H_5CH{=}N$	H	134–135	50–55	181–182[p]									
p-$NO_2C_6H_4CH{=}N$[o]	H	231.5–232.5	45	200–201[p]									
p-$(CH_3)_2NC_6H_4CH{=}N$[q]	H	177.5–178.5	10	212–213[p]									
OH[r]	H	211.5–212	90	197–198 (Lit. m.p. 188–189[s])	$C_{13}H_{10}O_2$	78.77	5.09			78.60	5.01		
H[t]	Br	165.5–166	87	169.5–170.5									
NH_2	Br	215.5–216[t]	100	204.5–205.5 (dec.)	$C_{13}H_{10}BrNO$	56.54	3.65	5.07	28.94	56.73	3.70	5.18	28.86
C_2H_5NH	Br	164.5–165.5[t]	90	137.5–138.5	$C_{13}H_{14}BrNO$	59.22	4.64	4.61		59.16	4.52	4.75	
n-C_3H_7NH	Br	108–108.5	100	143.5–144	$C_{16}H_{16}BrNO$	60.39	5.07	4.40	25.11	60.23	5.16	4.36	25.20
n-C_4H_9NH	Br	97–97.5	100	143–144	$C_{17}H_{18}BrNO$	61.45	5.46	4.22	24.05	61.52	5.50	4.09	24.02

TABLE I (*Continued*)

$C_6H_5CH_2NH$	Br	139–140	91	169.5–170.5	$C_{20}H_{16}BrNO$	65.58	4.40	3.83	21.82	65.54	4.57	3.67	21.68
p-$BrC_6H_4CH_2NH$	Br	159–160	100	174.5–175.5	$C_{20}H_{15}Br_2NO$	53.96	3.40	3.15	35.90	53.82	3.50	3.31	35.89
p-$NO_2C_6H_4CH_2NH$	Br	185–186	100	178.5–179	$C_{20}H_{15}BrN_2O_3$	58.41	3.68	6.81	19.43	58.15	3.40	6.93	19.52
$HOCH_2CH_2NH$[u]	Br	146–148	100	164–164.5 (dec.)	$C_{16}H_{14}BrNO_2$	56.27	4.41	4.38	24.96	56.20	4.80	4.32	25.46
$C_2H_5OOCCH_2NH$	Br	186–187	72	170.5–171.5 (slight dec.)	$C_{17}H_{16}BrNO_3$	56.37	4.45	3.87	22.06	56.38	4.73	3.77	22.20
CH_3CONH[t]	Br	271–271.5	100	256.5–257.5 (slight dec.)	$C_{15}H_{12}BrNO_2$	56.62	3.80	4.40	25.12	56.37	3.81	4.40	25.20

[a] Many of the substituted fluorenones were prepared by alkylating the aminofluorenone with alkyl bromide in triethyl phosphate or in dimethyl sulfoxide (Reference 3) or by alkyl phosphates in the presence of lithium bromide [T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955)]. The azomethines were prepared by condensation of the aminofluorenones with the corresponding aldehydes. Reports including preparation of these ketones are in progress. [b] Melting points are corrected. [c] W. Manser, Zurich; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; Mr. M. E. Taylor, this laboratory, and Weiler and Strauss, Oxford. [d] See Reference 4. [e] O. Diels, *Ber.*, **34**, 1758 (1901). [f] In diglyme. [g] See second reference in (a). [h] The 2-di-*n*-butylaminofluorenone was reduced as an oil. [i] Cyclopentylamino-. [j] In chloroform-methanol (2.5:1 by volume). [k] In methanol-diglyme (1:3 by volume). [l] Identical with the melting point (and mixture melting point) of the compound prepared by acetylation of 2-aminofluoren-9-ol (see Experimental). [m] The melting point of this ketone was erroneously reported as 245.5–246° (see second reference in *a*). [n] In dilute aqueous NaOH. [o] In chloroform-methanol (4:1 by volume) at 60°. [p] The mixture melting point with an authentic sample prepared by direct condensation of 2-aminofluoren-9-ol with the aldehydes (see Experimental) showed no depression. [q] With equimolar quantities of the ketone and sodium borohydride 88–94% of 2-*p*-dimethylaminobenzylaminofluoren-9-ol was obtained, m.p. 193.5–194.5°. *Anal.* Calcd. for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 80.30; H, 6.91; N, 8.49. [r] In water. This ketone was prepared by Mr. Murray E. Taylor of this laboratory. [s] See Reference 6. [t] See Reference 3. [u] This ketone was prepared by Mr. William H. Wetzel of this laboratory by hydroxyethylation of 2-amino-3-bromofluorenone with ethyl oxide. *Anal.* Calcd. for $C_{15}H_{14}BrNO_2$:N, 4.40; Br, 25.12. Found: N, 4.45; Br, 25.45.

selective reduction of the —N=CH— group in *N*-benzylideneaniline type Schiff bases with sodium borohydride in the presence of other reducible groups. We were interested, however, in determining the possibility of preservation of the —N=CHAr group with concomitant reduction of the carbonyl group.

In our study with a limited number of 2-*N*-aralkylideneaminofluorenones (Table II), we found that the reducibility of the —N=CH— group varies considerably. These differences were more evident in the reduction of 2-*N*-aralkylideneaminofluoren-9-ols. Equivalent amounts of 2-*N*-*p*-dimethylaminobenzylideneaminofluoren-9-ol and sodium-borohydride gave a high yield (80%) of the benzylaminofluoren-9-ol, whereas 2-*N*-*p*-nitrobenzylideneaminofluoren-9-ol, under the same conditions, gave a low yield (18%) of the reduced product. The reducibility of the —N=CH— group in 2-*N*-benzylideneamino-3-bromofluoren-9-ol is also low, as shown in Table II.

The reduction of the aralkylideneamino ketones presented a somewhat more complicated picture. Insolubility of the ketone was an obscuring factor in the room temperature reactions. However, Table II shows the same general picture with regard to preservation of the —N=CH— group. With 2-*N*-benzylideneaminofluorenone and the *p*-nitro derivative, the corresponding 9-fluorenol can be obtained conveniently in about 50% yield.

Reduction of 2-nitrofluorenone with sodium borohydride in the room temperature procedure gave a high-melting (>300°) yellow material instead of 2-nitrofluoren-9-ol.[6] We made the latter compound from 2-nitro-9-bromofluorene and anhydrous sodium acetate followed by acid hydrolysis. Reduction of 2-nitro-9-acetoxyfluorene with zinc and calcium chloride gave 2-amino-9-acetoxyfluorene. Acetylation of 2-aminofluoren-9-ol yielded 2-acetamidofluoren-9-ol or 2-acetamido-9-acetoxyfluorene depending on the conditions.

EXPERIMENTAL

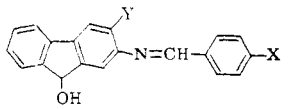
General procedure. To the ketone in methanol (magnetic stirrer), one-half mole equivalent of sodium borohydride was added in small portions over a period of 5 min. The resulting solution or suspension was continuously stirred for 5–25 min. (the temperature rose to 30° or slightly higher) and diluted with water. The precipitate was filtered, washed, dried, and recrystallized from a suitable solvent. (For alternative conditions see Tables I and II.)

2-Acetamidofluoren-9-ol. To a stirred hot solution of 2-aminofluoren-9-ol (9.9 g., 0.05 mole), in glacial acetic acid (100 ml.), a mixture of acetic anhydride (5.5 g., 0.054 mole) and acetic acid (30 ml.) was added in small portions (5 min.). Stirring was continued for another 10 min. then the reaction mixture was poured into cold water. The precipitate was filtered, washed with water and air dried,

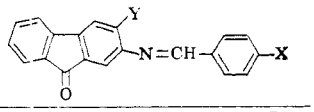
(6) C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 3977 (1954). The melting point of this compound was erroneously reported as 227° by E. A. C. Calderón, *Anales asoc. quím. arg.*, **36**, 19 (1948).

TABLE II

SUBSTITUTED 2-*N*-BENZYLAMINOFLUOREN-9-OLS (A) FROM 2-*N*-BENZYLIDENEAMINOFLUOREN-9-OLS (B) AND SUBSTITUTED (A) AND/OR (B) FROM THE CORRESPONDING 2-*N*-BENZYLIDENEAMINOFLUORENONES (C) BY SODIUM BOROHYDRIDE REDUCTION



X	Y	Molar Ratio, $NaBH_4$/B	Yield, %[a] A	% Unreacted, B
H	H	0.25	26–32	62–70
		1.00	90	—
$(CH_3)_2N$	H	0.25	80	18
		1.00	88	6
NO_2	H	0.25	18	79–82
		1.00	94	—
H	Br	0.25	—	88
		1.00	—	50



X	Y	Molar Ratio, $NaBH_4$/C	Yield, %[a] A	Yield, %[a] B	% Unreacted, C
H	H	0.25	8 (8[b])	52 (55[b])	4 (21[b])
		1.00	67	—	—
$(CH_3)_2N$	H	0.25	—	10	60
		1.00	88–94	—	—
NO_2	H	0.25	6 (3[c])	0 (45[c])	94 (50[c])
		1.00	13	—	78
H	Br	0.25	—	—	64
		1.00	—	—	29

[a] Only the yields of identified products are given. The first reaction in each pair was with equivalent quantities of ketone and sodium borohydride in methanol at a temperature of 30–35° (added heat was from magnetic stirrer) for 10 min. The second reaction was with equimolar reactants in methanol at 30–35° for 20 min. In all reactions, $NaBH_4$ was added in small portions over a period of 5 min. — Represents mixtures, difficult to purify. [b] Yield from the reaction in which $NBaH_4$ was added in one portion and the reaction mixture stirred as in (a) for 10 min. [c] Yield from the reaction in chloroform-methanol (4:1 by volume) at 50–60° for 5 min. The hydride was added in one portion.

yielding 11.7 g. (98%), m.p. 248.5–249°. Recrystallization from ethyl acetate-acetone gave short white needles, m.p. 249.5–250°.[7]

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48. Found: C, 75.46; H, 5.28.

2-Acetamido-9-acetoxyfluorene. A mixture of acetic anhydride (11.2 g., 0.11 mole), and pyridine (20 ml.) was added dropwise (10 min.) with constant agitation to a cooled (ice water) solution of 2-aminofluoren-9-ol (9.9 g., 0.05 mole) in pyridine (80 ml.). The reaction mixture was heated on a steam bath for 3 hr. then poured into cold water. The precipitate was filtered, washed with water, and dried, yielding 13.7 g. (97%), m.p. 223.5–228°. Recrystallization from acetic acid–ethanol gave white needles, 12.1 g. (86%), m.p. 227.5–228.5°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37. Found: C, 72.53; H, 5.61.

2-Nitro-9-acetoxyfluorene. A mixture of 2-nitro-9-bromofluorene (29 g., 0.1 mole) and anhydrous sodium acetate (27 g., 0.33 mole) in hot glacial acetic acid (300 ml.) was refluxed for 24 hr. The reaction solution was cooled to room temperature and the product was filtered, washed with water, and dried (18.5 g.). The acetic acid filtrate upon concentration gave a second crop of the product (8.0 g.). Recrystallization from acetone gave 24.8 g. (92%) of yellow needles, m.p. 155.5–156°.[8]

(7) J. A. Miller, R. B. Sandin, E. C. Miller, and H. P. Rusch, *Cancer Research*, **15**, 188 (1955). These authors reported the melting point of this compound as 240–241°. This perhaps contained some 2,9-diacetyl derivative.

(8) J. Schmidt and K. Bauer, *Ber.*, **38**, 3737 (1905).

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.73; H, 4.17; N, 5.20.

2-Nitrofluoren-9-ol. A solution of 2-nitro-9-acetoxyfluorene (5.4 g., 0.02 mole) in absolute ethanol (150 ml.) was refluxed 5 hr. with concentrated hydrochloric acid (15 ml.). After standing overnight at room temperature the mixture was heated and filtered. The filtrate was neutralized with dilute ammonia (1:1), a large quantity of water was added and the product filtered, washed, and dried. The yield was 4.3 g. (96%). Recrystallization from ethanol gave small yellow needles (4.2 g.), m.p. 126–126.5° (reported: 128–129°[6]).

Anal. Calcd. for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.17. Found: C, 68.42; H, 4.20; N, 6.00.

2-Amino-9-acetoxyfluorene. 2-Nitro-9-acetoxyfluorene (2.7 g., 0.01 mole) and zinc dust (4 g., 0.06 mole) were ground, stirred in 78% ethanol (200 ml.) and heated to boiling. A solution of anhydrous calcium chloride (3.3 g., 0.03 mole) in water (5 ml.) was then added. The mixture was refluxed with slow stirring for 4 hr. and filtered hot. The product isolated from the filtrate weighed 1.2 g. (50%), m.p. 124–125°. Recrystallization from ethanol-water gave shiny straw colored leaflets, m.p. 125–126°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.41; H, 5.76; N, 6.16.

2-N-Benzylideneaminofluoren-9-ol. A mixture of 2-aminofluoren-9-ol (3.9 g., 0.02 mole), benzaldehyde (5.3 g., 0.05 mole), and methanol (60 ml.) was boiled for 30 min. then cooled to room temperature. The product was filtered, washed with ethanol, and dried, yielding 5.2 g. (91%), m.p. 181–182°.

Anal. Calcd. for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91. Found: C, 84.26; H, 5.27; N, 5.01.

2-N-p-Dimethylaminobenzylideneaminofluoren-9-ol. To a boiling solution of 2-aminofluoren-9-ol (1 g., 0.005 mole) in 50% acetic acid (15 ml.), *p*-dimethylaminobenzaldehyde (0.76 g.) in 50% acetic acid (5 ml.) was added during a period of 5 min. The reaction solution was heated at 105–110° for 10 min. and diluted with an equal volume of water. The acid solution was rendered alkaline with concentrated ammonium hydroxide, and the product filtered and recrystallized from ethanol containing a small amount of acetic acid, yielding 1.2 g. (73%), m.p. 211–212°. Recrystallization from acetone gave m.p. 212–213°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14. Found: C, 80.67; H, 6.05.

2-N-p-Nitrobenzylideneaminofluoren-9-ol. To a boiling solution of 2-aminofluoren-9-ol (7.9 g., 0.04 mole) in absolute ethanol (250 ml.) containing a few drops of glacial acetic acid, *p*-nitrobenzaldehyde (6 g., 0.04 mole) in hot absolute ethanol (30 ml.) was added dropwise within 5 min. The reaction solution was then concentrated until crystallization of the product took place. After cooling to room temperature the shiny yellow plates were filtered, yielding 11.6 g. (88%), m.p. 200–201°.

Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.64; H, 4.44; N, 8.44.

2-N-Benzylideneamino-3-bromofluoren-9-ol. A mixture of 2-amino-3-bromofluoren-9-ol[3] (2.2 g., 0.008 mole), benzaldehyde (5.3 g., 0.05 mole), and glacial acetic acid (2 drops) was heated under reflux at 155–160° (bath) for 1 hr. and excess benzaldehyde removed under reduced pressure. The yellow solid residue was recrystallized from methanol giving 2.2 g. (76%) of light yellow needles, m.p. 175–178°. Two recrystallizations from methanol gave an analytical sample, m.p. 178.5–179.5°.

Anal. Calcd. for $C_{20}H_{12}BrNO$: C, 66.32; H, 3.34; N, 3.87. Found: C, 66.34; H, 3.89; N, 3.87.

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[CONTRIBUTION NO. 412 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENT STATION, E. I. DU PONT DE NEMOURS AND CO.]

Alkylidene Derivatives of 3-Pentenenitrile

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The synthesis of nine new alkylidene derivatives of 3-pentenenitrile (1-substituted-2-cyano-4-methyl-1,3-butadienes) by the condensation of 3-pentenenitrile with aldehydes and ketones is described. The compounds derived from aldehydes form low molecular weight polymers on heating.

The Knoevenagel modification of the Perkin reaction has been used previously to prepare unsaturated acids or nitriles by condensation of aldehydes or ketones with such active methylene compounds as phenylacetic acid, malonic acid, cyanoacetic acid, and benzyl cyanide in the presence of alkaline reagents.[1] Cope[2] prepared a series of alkylidene cyanoacetic esters, $R_1R_2C{=}C(CN)\text{-}COOCH_3$, by condensing ketones with methyl cyanoacetate and interpreted the experimental evidence in favor of an aldol-type mechanism for the Knoevenagel reaction.

Compounds in which a methylene group is activated by a double bond and a nitrile group have now been found to undergo this reaction. Alkylidene derivatives of 3-pentenenitrile have been synthesized by condensation of aldehydes and ketones with 3-pentenenitrile, prepared by reaction of butadiene with hydrogen cyanide, in the presence of sodium alkoxides. The mechanism is similar to that proposed by Cope:[2] (*1*) formation of a carbanion of the 3-pentenenitrile, probably through dissociation of a hydrogen ion,

$$CH_3CH{=}CHCH_2CN \rightleftharpoons H^+ + [CH_3CH{=}CHCH(CN)]^-;$$

(*2*) addition of the carbanion to the carbonyl compound,

$$R_1R_2C{=}O + [CH_3CH{=}CHCH(CN)]^- + H^+ \rightleftharpoons CH_3CH{=}CHCH(CN)\underset{\displaystyle OH}{\underset{|}{C}}R_1R_2;$$

and (*3*) elimination of water from the aldol-like intermediate,

$$CH_3CH{=}CHCH(CN)\underset{\displaystyle OH}{\underset{|}{C}}R_1R_2 \rightleftharpoons CH_3CH{=}CHC(CN){=}CR_1R_2 + H_2O.$$
$$\text{A}$$

The physical properties of the 2-alkylidene derivatives of 3-pentenenitrile are summarized in the table.

Structural assignment was based on elemental analysis, infrared and ultraviolet absorption, the high exaltation in molecular refraction, and the formation of a crystalline dibromide to which the structure, $CH_3CHBrCHBrC(CN){=}CR_1R_2$,[3,4] was assigned.

(1) J. R. Johnson, *Org. Reactions*, **1**, 210 (1947).

(2) A. C. Cope, *J. Am. Chem. Soc.*, **59**, 2327 (1937).

(3) Mahan, U. S. Patent **2,384,630** (1945), describes an analytical method based on the fact that 3-pentenenitrile adds bromine whereas 2-pentenenitrile does not add bromine.

(4) Linstead, *J. Chem. Soc.*, 358 (1927), reports that bromine adds to $\beta\gamma$-unsaturated acids about 100 times faster than to $\alpha\beta$-unsaturated acids.