

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

## Derivatives of Fluorene. IV. Raney Nickel-Hydrazine Hydrate Reduction of Various Mono- and Dinitrofluorene Derivatives; Some New 9-Substituted Fluorenes<sup>1</sup>

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A Raney nickel-hydrazine hydrate method for reducing aromatic nitro groups has been extended to fluorene derivatives including those having  $>C=O$ ,  $>C=C<$ ,  $NHCOCF_3$  and other functional groups, and dinitro compounds. For the less soluble substances, certain specific directions must be followed, but most yields were 90% or higher and the first crop out of the reaction mixture was of good quality. A nitro compound with an azomethine linkage gave a product with both functions reduced. Some new substances are described.

The convenient steam bath reduction, in excellent yields, of some aromatic nitro compounds to amines with Raney nickel and hydrazine hydrate in ethanol was reported by Balcom and Furst.<sup>2</sup> Since then, a few reports<sup>3,4</sup> have appeared in which this method has been tried on one or two nitro compounds with good results, after failure or poor results with other methods.

This work is presented because there have been several recent reports of reduction of nitrated derivatives of fluorene in poor yield or by methods more tedious than this, because we have found this reaction, with few exceptions, thoroughly satisfactory, and because in certain of the procedures, notably with dinitro compounds and fluorenone derivatives, simple but necessary precautions must be observed.

It was found,<sup>5</sup> and confirmed,<sup>2</sup> that without a catalyst nitro compounds did not undergo reduction at room temperature. Some can be reduced to the amine in refluxing alcohol by hydrazine hydrate alone<sup>6</sup> but yields are often low and the reaction is slow. Higher temperatures often lead to side reactions. Recently, reduction with palladized charcoal and hydrazine hydrate was reported.<sup>7</sup> Yields,

with one exception, ranged from 60 to 68%, whereas yields with Raney nickel, at a comparable state of purity, are from 80 to 95% (mostly 90% and above). Furthermore, it is stated that the reduction with palladized charcoal is successful only with "activated" nitro groups. We have found no such limitation with Raney nickel.

Mono- and dinitrofluorenes and ring-substituted derivatives of these (with amino, dimethylamino, acetamido, trifluoroacetamido, iodo and *p*-tosylamido groups) have been readily reduced in this laboratory with 3 to 4 or more molar equivalents per nitro group of 100% hydrazine hydrate<sup>8</sup> (64%  $N_2H_4$ ) and catalytic amounts of Raney nickel.<sup>9</sup>

The factor limiting batch size with many of the nitro compounds was solubility<sup>10</sup> and we found that toluene, with sufficient ethanol to insure initial complete miscibility of the hydrazine hydrate, gives fully as satisfactory reductions as ethanol alone.

Balcom and Furst<sup>2</sup> reported that the carbonyl groups of the compounds they used were not affected. This is essentially correct in our experience, but we have found that reduction of 2-nitrofluorenone gives us a very small but consistent (3%) yield of 2-amino-9-fluorenone. Prolongation of the reaction time does not raise this yield and there is no 2-nitro-9-fluorenone in the starting material. In the case of the compound cited, even this small amount of 9-ol was sufficient to give us 2-amino-9-fluorenone of apparent poor quality until, its presence realized, we learned how to separate the 9-ol and allow recovery of 90-94% yields of pure 2-aminofluorenone. In this reduction we have also

(1) This investigation was supported in part by research grant C-1744 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service. For preceding publications in this series see: (a) M. E. Taylor and T. L. Fletcher, *J. Org. Chem.*, **21**, 523 (1956); (b) T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955).

(2) D. Balcom and A. Furst, *J. Am. Chem. Soc.*, **75**, 4334 (1953). These investigators reported that reduction also takes place at room temperature, but with most of our substances low solubility made steam bath temperatures necessary. See A. Furst and R. E. Moore, *J. Am. Chem. Soc.*, **79**, 5492 (1957) for further observations.

(3) D. S. Tarbell, R. F. Smith, and V. Boekelheide, *J. Am. Chem. Soc.*, **76**, 2470 (1954).

(4) R. K. Brown and N. A. Nelson, *J. Am. Chem. Soc.*, **76**, 5149 (1954).

(5) L. P. Kuhn, *J. Am. Chem. Soc.*, **73**, 1510 (1951).

(6) R. Möhlau, H. Beyschlag, and H. Köhres, *Ber.*, **45**, 133 (1912).

(7) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 2556 (1956).

(8) Obtained from the Mathieson Chemical Corp., Baltimore, Md. This company generously donated some of this material at the beginning of our work.

(9) See C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1635 (1956) and footnotes, for reference to alkylation of primary aromatic amines with alcohols and (relatively) large amounts of Raney nickel. In this connection see also G. N. Kao, B. D. Tilah, and K. Venkataraman, *J. Sci. Ind. Research (India)*, **14B**, 624 (1955).

(10) We have successfully reduced 2-nitrofluorene in an amount of alcohol insufficient to effect complete solution. This variation is not successful with less soluble compounds.

TABLE I  
 RANEY NICKEL-HYDRAZINE HYDRATE REDUCTION OF SOME AROMATIC NITRO COMPOUNDS

Nitro Compounds <sup>a</sup>	Mole	Products	Yield, %	M.P., °C.	Calcd.	Analyses, %		Calcd.	N Found	
						C Found	H Found			
Fluorenes										
2-Tosylamido-3-nitro-(T,A) <sup>b</sup>	0.01	2-Tosylamido-3-amino-	90-95	200-201					8.00	8.00
2-Amino-3-nitro-(A) <sup>c</sup>	0.01	2,3-Diamino-	90	191-193 (193) <sup>e</sup>						
2-Acetamido-3-nitro-(T,A) <sup>b</sup>	0.01	2-Acetamido-3-amino-	90	235-237 (225-227) <sup>i</sup>	75.60	75.89	5.92	6.19	11.76	11.74
2-Amino-7-nitro-(T,A) <sup>b</sup>	0.05	2,7-Diamino-	90	164-165 (165) <sup>g</sup>					14.28	14.42
2-Acetamido-7-nitro-(A) <sup>b</sup>	0.05	2-Acetamido-7-amino-	90-95	200-202 (198-199) <sup>m</sup>						
2-Trifluoroacetamido-7-nitro-(T,A) <sup>d</sup>	0.05	2-Trifluoroacetamido-7-amino-	90	201-202	61.64	61.63	3.77	3.87	9.58	9.65
2-Dimethylamino-3-nitro-(A) <sup>b</sup>	0.1	2-Dimethylamino-3-amino-	85-90	155-156	80.32	80.41	7.19	7.14	12.49	12.43
2-Dimethylamino-7-nitro-(A) <sup>e</sup>	0.01	2-Dimethylamino-7-amino-	80	147-148	80.32	80.55	7.19	7.37	12.49	12.66
2-Iodo-7-nitro-(A) <sup>f</sup>	0.01	2-Iodo-7-amino-	85	159-161 (158-160) <sup>f</sup>						
2,7-Dinitro-(T,A) <sup>g</sup>	0.01	2,7-Diamino-	95-97	164-165 (165) <sup>g</sup>						
2,5-Dinitro-9-oxo-(T,A) <sup>g</sup>	0.01	2,5-Diamino-9-oxo-	85-90	200.5-203 (200) <sup>n</sup>	74.27	74.14	4.79	4.99	13.33	13.48
2-Nitro-9-morpholino-(A)	0.05	2-Amino-9-morpholino-	95-97	229-230					10.52	10.58
2-Nitro-9-benzylidene-(T,A) <sup>h</sup>	0.01	2-Amino-9-benzylidene-	80-85	105-121 (105-130) <sup>h</sup>	89.18	89.18	5.61	5.73	5.20	5.25
2-Nitro-9-biphenylylimino-(T,A) <sup>i</sup>	0.01	2-Amino-9-biphenylylimino-	95	164-165					8.04	8.16
QUINOLINES										
6-Nitro-(A) <sup>j</sup>	0.01	6-Amino-	90-95	115-115.5 (114) <sup>j</sup>						
8-Nitro-(A) <sup>k</sup>	0.01	8-Amino-	90-95	63-64 (64-65) <sup>k</sup>						

<sup>a</sup> T (toluene), A (ethanol) following the compound name signifies the reaction solvent used. <sup>b</sup> F. Bell and D. B. Mulholland, *J. Chem. Soc.*, 2020 (1949), 2-Tosylamido-3-nitrofluorene was synthesized by Mr. M. E. Taylor and Mr. W. H. Wetzel of this laboratory in another connection. <sup>c</sup> O. Diels *et al.*, *Ber.*, 35, 3286 (1902). <sup>d</sup> From 2-amino-7-nitrofluorene and trifluoroacetic anhydride in benzene, m.p. 201-201.5°. *Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>: C, 55.91; H, 2.82; N, 8.69. Found: C, 56.03; H, 3.05; N, 8.58. <sup>e</sup> From 2-amino-7-nitrofluorene and trimethyl phosphate in the presence of an equivalent of lithium bromide (see<sup>1b</sup>), m.p. 229-230°. *Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.75; H, 5.70; N, 10.80. <sup>f</sup> E. K. Weisburger, *J. Am. Chem. Soc.*, 72, 1758 (1950). <sup>g</sup> G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, 2691 (1926). <sup>h</sup> See<sup>1a</sup>. <sup>i</sup> See<sup>11</sup>. <sup>j</sup> F. Linsker and R. L. Evans, *J. Am. Chem. Soc.*, 68, 874 (1946). <sup>k</sup> L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, 62, 1644 (1940). <sup>l</sup> H. R. Gutmann and S. W. Fenton, *J. Am. Chem. Soc.*, 77, 4422 (1955). <sup>m</sup> S. Schulman, *J. Org. Chem.*, 14, 382 (1949). <sup>n</sup> C. Courtot, *Compt. rend.*, 217, 453 (1943).

recovered 1-2% of 2,2'-azoxyfluorenone. Slight alteration of the procedure described below (such as too high a concentration of the nitro compound, use of Raney nickel prepared more than a few weeks previously, insufficient hydrazine hydrate or nickel, or insufficient initial heating) has given us a much higher yield of the azoxy compound together with a mixture of other high melting substances. With all of the nitrofluorenone derivatives, the presence of some Raney nickel at the time the hydrazine hydrate is added seems essential (perhaps to prevent hydrazone and/or ketazine formation) for a high yield of good amine. In addition, for dinitro com-

pounds and, in general, for substances with low solubility, initial application of sufficient heat is mandatory (see Experimental).

We have also tried this reduction on several different types of 9-substituted fluorenes. With 2-nitro-9-morpholinofluorene, obtained by interaction of 2-nitro-9-bromofluorene with morpholine, poor results were obtained until the amount of hydrazine hydrate was increased to at least 5 equivalents. The product was identical with that from hydrolysis of 2-trifluoroacetamido-9-morpholinofluorene.

The *cis-trans* mixture of 2-nitro-9-benzylidene-

fluorenes described by Bergmann *et al.*<sup>11</sup> was reduced with 8 molar equivalents of hydrazine hydrate to the corresponding mixture of 2-amino-9-benzylidene fluorenes<sup>11</sup> in good yield, but with three equivalents of the hydrazine hydrate a mixture of two substances resulted: one compound, with high melting point, had correct analyses for 2,2'-azoxy-9,9'-benzylidene fluorene; the other, lower melting, was thought at first to be a stereoisomer but analyses were not compatible with this structure.

It has been reported<sup>12</sup> that the aryl  $\text{—C}\equiv\text{N}$  group is partially reduced under these conditions (upon hydrolysis of the product, the corresponding aldehyde is obtained), and that a nitropyrimidine was not successfully reduced.<sup>13</sup> As an extension, to substances containing a formal unsaturated carbon to nitrogen linkage, we found that 6-nitro and 8-nitroquinoline each gave a high yield of the corresponding amine. However, when we tried this reaction with a 9-arylimino fluorene, 2-nitro-9-*p*-biphenylylimino fluorene<sup>1a</sup>, and five equivalents of hydrazine hydrate, we observed a sluggish reaction and, after 10 minutes, added another five equivalents. A brisk foaming took place and after the customary time on the steam bath we obtained a good yield of 2-amino-9-*p*-biphenylylamino fluorene.

New data on the preparation and purification of 2,5-dinitrofluorene is presented in the experimental section. This substance has been reported as melting at 207°<sup>14</sup> and is commonly used melting at 205–206°. In this stage the compound is contaminated with 2,7-dinitrofluorene and at least one other substance. We observed discoloration upon melting 2,5-dinitrofluorene of the usual purity, and inconsistent or poor reductions with Raney nickel and hydrazine hydrate. Attempts to purify the compound by repeated crystallization from acetic acid or toluene raised the melting point to 210–211° but the product still contained a small amount of high-melting material. The procedure described below gave us the dinitro compound melting at 214.5–215.5°. After storage in the dark for one year, the melting point was the same.<sup>15</sup>

#### EXPERIMENTAL<sup>16</sup>

Description of two typical reductions follows, and procedures leading to some new compounds.

*2-Amino fluorene.* A solution of 105.5 g. (0.5 mole) of 2-

nitrofluorene<sup>17</sup> in 1500 ml. of toluene and 500 ml. of 95% ethanol was heated almost to boiling in a 6-l. Erlenmeyer flask. We used a 4-l. flask, but this requires considerable care at the beginning to prevent loss by foaming. The flask was then transferred to the steam bath and 70 ml. (~3 moles) of 100% hydrazine hydrate<sup>8</sup> were carefully added with thorough mixing. Immediately thereafter, Raney nickel<sup>18</sup> was cautiously added with mixing. Heating was continued for 40 min. with addition of a small amount of catalyst 15–20 min. after the start of the reaction.<sup>19</sup> The mixture was then boiled down in the presence of a small amount of fresh Raney nickel (and boiling chips) and when alkaline vapors no longer came off, the solution was filtered and the filtrate boiled down to about 300 ml. After slight cooling, 100 ml. of ethanol was carefully added with mixing. A mass of white crystals came out. Cooling, filtration, and drying gave 86 g. (95%) of amine, m.p. 127–128°. A second crop of about 3.5 g. was recovered (~4%), m.p. 125–127°. The material in the first crop is sufficiently pure for most work. One crystallization from ethanol (82 g. from 86 g.) raised the m.p. to 128–129°. Smaller amounts of 2-nitrofluorene can be reduced conveniently in alcohol alone.

*2-Amino fluorenone.* To a solution of 15 g. (0.066 mole) of 2-nitrofluorenone (from toluene<sup>1b</sup>) in 1 l. of toluene and 300 ml. of ethanol in a 3-l. Erlenmeyer flask, a small amount of Raney nickel was added and, with the solution just under boiling, 12 ml. of hydrazine hydrate, with thorough mixing, followed by more catalyst. The mixture was then brought to a vigorous boil and lowered into the steam bath under an Allihn condenser fitted with a cork. After 15–20 min. catalyst was added and after 30 min., the solution having become a clear red, boiling chips and more catalyst were added and the mixture boiled down until the vapors were no longer alkaline. Decomposition of all the hydrazine is necessary before filtering, otherwise by-products are formed. After filtration and washing of the filter with hot toluene, the solution was boiled almost to dryness and allowed to stand for 1 hr. The solid was then taken up in 400 ml. of 95% ethanol (alternatively, from this point on, 6 to 12 reductions were combined and worked up identically), and warmed on the steam bath to effect solution. Filtration removed a small amount of highly insoluble orange-colored azoxyfluorenone; the amount (from 15 g. of the nitro compound) varied from none detectable to ~0.3 g. The filter was washed with warm alcohol and the solution boiled down to 160 ml. and allowed to stand until crystallization was complete. The first crop amounted to 9.6 g. (74%), m.p. 159–161°. Upon reducing the filtrate to 60–70 ml., a further 1.8 g. was removed (14%), m.p. 157–160°. Both crops were recrystallized from

(16) Melting points are corrected. Analyses were made by W. Manser, Zurich, Switzerland; Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y., and (some of the nitrogens) by Mr. M. E. Taylor of this laboratory.

(17) Prepared in the usual way (see W. E. Kuhn in *Org. Syntheses*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 447), but much more conveniently in a large beaker in 250-g. batches. The product is filtered, washed, crystallized from acetic acid and, to remove traces of acetic acid, recrystallized from toluene.

(18) This amount (0.5–0.6 g. dried) was three times that conveniently transferred (from ethanol) on the end of a spatula having a blade 65 mm. wide. The nickel was prepared as described in the chapter by R. Schröter in *Newer Methods of Preparative Organic Chemistry*, Interscience, New York, N. Y., 1948, p. 65. It appears to lose its efficiency after a few weeks especially with 2-nitrofluorenone and 2,5-dinitrofluorene.

(19) Occasionally a yellow color has persisted in the mixture as long as 0.5 hr. and, if allowed to remain, the product (in slightly lower yield) is yellow. In such cases we have added another 15 ml. of hydrazine hydrate with some Raney nickel and kept the mixture on the steam bath another 15–20 min.

(11) E. D. Bergmann, B. Pullman, and Y. Sprinzak, *Bull. soc. chim. biol.*, **34**, 586 (1952).

(12) S. Pietra and C. Trincherà, *Gazz. chim. ital.*, **85**, 1705 (1955).

(13) P. E. Fanta and E. A. Hedman, *J. Am. Chem. Soc.*, **78**, 1424 (1956).

(14) E. D. Hughes, C. G. LeFèvre, and R. J. W. LeFèvre, *J. Chem. Soc.*, 202 (1937).

(15) See footnote 16 in J. H. Weisburger, E. K. Weisburger, and H. P. Morris, *J. Am. Chem. Soc.*, **74**, 4540 (1952), regarding stability of 2,5-dinitrofluorene as generally used.

a small amount of toluene with almost quantitative recovery, m.p. 160.5–162° (analytically pure). A third crop was boiled with hydrochloric acid (1 part acid plus 10 parts water) in a ratio of 500 ml. acid to 10 g., and filtered hot. The filtrate deposited yellow needles of the hydrochloride of 2-aminofluorenone<sup>20</sup> (a further 3–4% of good quality amine). The acid solution, after separation of the preceding, was made alkaline and the precipitate dried and recrystallized from alcohol giving ~3% of 2-amino-9-fluorenone, m.p. 200.5–201° (lit.<sup>21</sup> m.p. 200°; mixture melting point with authentic sample undepressed).

*2,2'-Azoxyfluorenone.*<sup>22</sup> The orange compound resulting above was extremely insoluble in all solvents tried. It was purified by extraction with hot toluene followed by acetone, m.p. > 330° dec.

*Anal.* Calcd. for C<sub>26</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 77.60; H, 3.51; N, 6.96. Found: C, 77.84; H, 3.66; N, 7.10.

*2,5-Diaminofluorene.* Fluorene (100 g.) was dinitrated in the usual way (see Table<sup>9</sup>). The crude product was washed with cold acetic acid, cold alcohol and water, dried, and extracted by boiling with 750 ml. of acetic acid, filtering hot, and then with a further 500 ml., again filtering hot. The combined filtrates were boiled down and the first crop was recrystallized from acetic acid (m.p. 206–208°, with slight residue and discoloration). At this stage several runs were combined and taken up in nitrobenzene<sup>23</sup> (500 ml. to 75 g.) warmed to 120° to effect solution, allowed to cool, and the precipitated crystals filtered off and washed with cold alcohol. Recrystallization from toluene (Darco) and then chloroform served to raise the m.p. to 212–213.5° with no residue and no discoloration. This material was analytically pure and used for further work. However, recrystallization from acetic acid then toluene gave m.p. 214.5–215.5° (lit. 207°<sup>14</sup>).

The dinitro compound (8.6 g., 0.033 mole) was dissolved in a mixture of 1200 ml. of toluene and 400 ml. of ethanol and reduced with 30 ml. (~10 equivalents per nitro group) of hydrazine hydrate in the usual way, but with the initial boiling period lengthened to 5 min. beginning at the time of addition. Reflux was not necessary. After 0.5 hr. the solution was boiled down (fresh catalyst), filtered, and further taken to small volume; yield 6.2 g. (95%), m.p. 175.5–176.5°. Recrystallization from toluene gave 6.0 g., m.p. 176.5–177° (lit.<sup>24</sup> m.p. 177–178.5°). A small second crop was also recovered.

*Anal.* Calcd. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>: C, 79.56; H, 6.16; N, 14.28. Found: C, 79.57; H, 6.04; N, 14.37.

Acetylation gave 2,5-diacetamidofluorene which after two crystallizations from acetic acid melted at 301–302° corr. (lit.<sup>25</sup> m.p. 296°).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.84; H, 5.75. Found: C, 73.07; H, 5.70.

(20) This method of separation had been worked out in another connection by Mr. M. E. Taylor of this laboratory.

(21) O. Diels, *Ber.* 34, 1758 (1901).

(22) Use of impure 2-nitrofluorene or insufficient hydrazine hydrate gave the known 2,2'-azoxyfluorene in good yield.

(23) We obtained a clearer product if, instead of using commercial nitrobenzene, we first treated it with dilute sodium carbonate solution, then dilute sulfuric acid followed by water washing and drying.

(24) J. H. Weisburger and E. K. Weisburger, *J. Org. Chem.*, 21, 514 (1956).

(25) E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, 20, 1396 (1955).

*9-Morpholino-2-nitrofluorene.* Equivalent quantities of 9-bromo-2-nitrofluorene and morpholine were heated together under reflux in a small amount of methanol for 30 min. and the reaction mixture filtered from a small amount of reddish-orange material (probably 2,2'-dinitrobifluorenylidene) stirring into dilute potassium carbonate solution. Filtration and drying gave 95–98% yields. Recrystallization from methanol (Darco) gave cream-colored needles, m.p. 150–151.5°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: N, 9.45. Found: N, 9.52.

*9-Morpholino-2-trifluoroacetamidofluorene.* Morpholine (2 equivalents) and 9-bromo-2-trifluoroacetamidofluorene<sup>26</sup> were heated under reflux in ethanol and stirred into cold dilute potassium carbonate. The dried product was treated in benzene with Darco, filtered, and boiled down to small volume. The resulting crystals were dried and recrystallized from methanol giving 85% yields. One more crystallization from alcohol gave a pure sample, m.p. 209–209.5°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C, 62.98; H, 4.73; N, 7.73. Found: C, 62.91; H, 4.75; N, 7.82.

*2-Amino-9-morpholinofluorene.* A portion of the stirred suspension of the above reaction mixture (dilute potassium carbonate) was boiled gently in a covered beaker for 2 hr., replacing the water occasionally, and filtered. The dried material yielded (methanol) white crystals identical with the product from reduction of 2-nitro-9-morpholinofluorene (melting point and mixture melting point, see Table I).

*2-Acetamido-9-morpholinofluorene.* Acetylation of the latter compound gave a quantitative yield, m.p. 234–235°. One crystallization from methanol (Darco), m.p. 236–236.5°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.00; H, 6.54; N, 9.09. Found: C, 73.96; H, 6.79; N, 9.14.

*2,2'-Azoxy-9,9'-dibenzylidene fluorene(?)*. When three equivalents of hydrazine hydrate were used in the reduction of the 2-nitro-9-benzylidene fluorene (*cis* and *trans* mixture, Table I), the product consisted of two substances. One, obtained by extraction with alcohol and recrystallization from benzene (light yellow needles), melted at 182.5–184° and has not been identified. The other, a residue from the above extraction was recrystallized three times from benzene (yellow needles), m.p. 244.5–247.5°.

*Anal.* Calcd. for C<sub>40</sub>H<sub>28</sub>N<sub>2</sub>O: C, 87.25; H, 4.76; N, 5.09. Found: C, 87.60; H, 4.69; N, 5.11.

*2-Acetamido-9-(N-acetyl)-p-biphenylaminofluorene.* Attempted acid hydrolysis of the reduction product from 2-nitro-9-biphenyliminofluorene (Table I) returned the starting material quantitatively. Acetylation gave a diacetylated product, m.p. 132–133°, from alcohol-water.

*Anal.* Calcd. for C<sub>29</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 80.53; H, 5.59. For the monoacetyl compound: C, 83.43; H, 5.19. Found: C, 80.94; H, 5.78.

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(26) From 16 g. (0.09 mole) of *N*-bromosuccinimide and 22 g. (0.08 mole) of 2-trifluoroacetamidofluorene in 850 ml. of refluxing benzene with ultraviolet illumination for 4 hr. The solution was cooled to 50–60°, extracted with several portions of water, dried over sodium sulfate, and the benzene distilled off. The residue was then dried on the steam bath (air current), and the product recrystallized with filtration from carbon tetrachloride 75–80% yields, m.p. 181–183°. One more crystallization gave an analytical sample, m.p. 182–183°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>BrF<sub>3</sub>NO: C, 50.59; H, 2.55. Found: C, 50.68; H, 2.52. This preparation was first carried out by Mr. H. L. Pan of this laboratory in another connection.