ceased (no more refluxing liquid), and the desired ether could be isolated by addition of water; yield, 16.5 g. (61%); b.p. 106°.

2-Bromo-1,1,2-trifluoroethyl n-propyl ether. In the same manner, the reaction between 16 g. of bromotrifluoroethylene in 25 ml. of *n*-propyl alcohol and 0.5 g. of sodium in 20 ml. of propanol was carried out. The temperature rose spontaneously to 77°. The propanol was removed *in vacuo* and the product purified by distillation, b.p. 76° (130 mm.); yield, 16 g. (73%).

2,2-Dibromo-1,1-difluoroethyl methyl ether. In the manner described above, a few drops of a solution of 0.25 g. of sodium in 10 ml. of methanol were added to a solution of 25 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of methanol. A lively exothermic reaction took place. The balance of the sodium methoxide solution was added with cooling so that the temperature of the mixture did not exceed 40°. The ether was isolated by addition of water, dried and distilled, b.p. 55.8° (30 mm.); yield, 22 g. (77%).

2,2-Dibromo-1,1-difluoroethyl ethyl ether. To a solution of 24 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of alcohol, a solution of 0.5 g. of sodium in 20 ml. of ethanol was added, until further addition did not cause any more rise in temperature. Water was added and the ether dried over calcium chloride and distilled. It boiled at 65° (26 mm.); yield, 23 g. (79%).

2,2-Dibromo-1,1-difluoroethyl n-propyl ether. The reaction between 23 g. of 1,1-dibromo-2,2-difluoroethylene in 30 ml. of *n*-propyl alcohol and 0.5 g. of sodium in 20 ml. of the same solvent was carried out as in the foregoing case. The reaction was completed by heating the mixture at 90° for 30 min. and the excess *n*-propanol removed under reduced pressure. The product boiled at 72° (23 mm.); yield, 21 g. (72%).

With *isopropanol*, no reaction took place under the same operating conditions.

2-Bromo-1,1-difluoroethyl methyl ether. At −15°, a solution of 0.5 g. of sodium in 20 ml. of methanol was added to a solution of 20 g. of 1-bromo-2,2-difluoroethylene in 25 ml. of methanol. The mixture was slowly brought to room temperature and kept until the reflux ceased. As the product forms an azeotrope with methanol, it was precipitated by addition of water, dried and distilled; yield, 13.5 g. (61%). It boiled at 98° (760 mm.) or 58° (210 mm.). Upon standing for 4 days, it began to decompose and liberated hydrogen fluoride; at this stage, it had become impossible to distill the product without complete decomposition.

2-Bromo-1,1-difluoroethyl ethyl ether. In the same manner, the ethyl ether (b.p. 70° (175 mm.); yield, 12 g. (60%)) was obtained from 16.8 g. of 1-bromo-2,2-difluoro-ethylene in 25 ml. of alcohol and 0.5 g. of sodium in 20 ml. of ethanol. The product showed the same behavior as the methyl ether.

TEL-AVIV, ISRAEL

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

Derivatives of Fluorene. VIII. Fluorofluorenes. II[1]

T. LLOYD FLETCHER, MOSES J. NAMKUNG, HSI-LUNG PAN, AND WILLIAM H. WETZEL

Received December 3, 1959

Further work is reported concerning ring-fluorinated 2-acetamidofluorene (a carcinogen), and related compounds. Improved preparation of the 4- and 5-fluoro isomers is described together with preparation of the new 1-fluoro and 8-fluoro-2-acetamidofluorenes. Monodemethylation of the $-N(CH_3)_2$ group is encountered in an attempted Schiemann decomposition. Some observations concerning the directive effect of substituent fluorine in nitration of the fluorene nucleus are noted.

This paper describes the preparation of further new *N*-2-(monofluorofluorenyl)acetamides[2] and related compounds, and better methods for some previously reported members of this series.

We have found the following method preferable for making *N*-2-(4-fluoro-fluorenyl)acetamide, a compound described in the previous paper in this series.[1] *m*-Nitroaniline was iodinated by modification of a known procedure.[3] The diazonium fluoborate of this substance gave the corresponding fluoro compound. The yield in this step was improved from very poor to above 40% by rapid heating (170°) in sand under aspirator vacuum. Lower temperatures and longer time, which had improved yields in some of our decompositions, led to greatly increased tar formation—perhaps because of the substituent iodine. An Ullmann reaction followed by hydrolysis, separation and cyclization gave 4-fluoro-2-nitrofluorenone. Reduction of the nitro group[1] and then of the 9-keto followed by acetylation, all as described in the Experimental section, yielded the desired product.

In an improved approach to the 2,5-isomer we began with 4-carboxyfluorenone[1] and, by way of the known acid chloride, azide and 4-aminofluorenone, obtained fluorenone-4-diazonium fluoborate. When this was decomposed in sand, 60% yields of 4-fluorofluorenone were recovered, but when heated in suspension in toluene (in this case at 60–65°), 70% yields were obtained with much greater convenience. Reduction gave the known 4-fluorofluorene.[1]

Use of a liquid medium in decomposing diazonium fluoborates is not new, but suspension in benzene, toluene, xylene,[4] chloro-, or bromo-

---

[1] This work was supported in part by a grant (C-1744) from the National Cancer Institute, U. S. Public Health Service. For the preceding paper in the fluorofluorene series see *J. Am. Chem. Soc.*, **81**, 1092 (1959).

[2] These compounds are being tested for carcinogenicity and in metabolic studies by Drs. J. A. and E. C. Miller at the McArdle Memorial Laboratory, The University of Wisconsin.

[3] M. P. Brenans and M. A. Haller, *Compt. rend.*, **138**, 1503 (1904).

[4] A. Roe and G. F. Hawkins, *J. Am. Chem. Soc.*, **71**, 1785 (1949). A. Roe, *Organic Reactions*, Vol. V, John Wiley and Sons, New York, N. Y., 1949, p. 211.

benzene[5] does not seem to have been used as extensively as the great convenience of the method would suggest. We have also used *o*-dichlorobenzene successfully with substances having a decomposition point too high for boiling xylene.

Nitration of 4-fluorofluorenone in 60–65% yield, reduction to the amine and carbonyl reduction with phosphorus and hydriodic acid gave the known[1] 5-fluoro-2-fluorenamine.

Preparation of the first of the new fluorinated 2-acetamidofluorenes to be described here started with nitration[6] of fluorene-1-carboxylic acid (obtained by oxidation of fluoranthene and reduction of the 9-oxofluorene-1-carboxylic acid with phosphorus and hydriodic acid[7]) to 7-nitrofluorene-1-carboxylic acid. A Schmidt reaction gave known 7-nitro-1-fluorenamine. The diazonium fluoborate of the latter, made in the presence of phosphoric acid[8] and decomposition in toluene, gave 1-fluoro-7-nitrofluorene, which was reduced[9] and acetylated to form *N*-2-(8-fluorofluorenyl)acetamide. Alternatively, we prepared 1-amino-fluorenone from 1-acetamidofluorenone.[10] A Schiemann reaction gave 1-fluorofluorenone, which was nitrated in the 7- position; this proved to be identical with the product obtained from oxidation of 1-fluoro-7-nitrofluorene with sodium dichromate. Reduction to the amine was followed by attempted reduction of the 9-carbonyl. This proved disappointing and the method was abandoned.

Trifluoroacetylation of 1-fluoro-7-fluorenamine, followed by nitration, led to a high yield of the 2-nitro derivative.[11] Mild alkaline hydrolysis and deamination gave 1-fluoro-2-nitrofluorene, which we reduced and acetylated to obtain *N*-2-(1-fluorofluorenyl)acetamide, identical (melting point, mixture melting point and infrared spectrum) with a by-product obtained in small yield from a reaction sequence which had given us the 3-fluoro-2-nitro- isomer.[12] The by-product, as is shown in the work cited, could only be from the alternate product of cyclodehydration, *i.e.*, the 1-fluoro-2-nitrofluorenone. Oxidation of 1-fluoro-2-nitrofluorene with sodium dichromate gave a fluorenone identical (infrared spectrum) with a compound described as 1-fluoro-2-nitrofluorenone.[13]

Observations of Bergmann *et al.*,[14] regarding the "unusually large reactivity of the *ortho*-position" (to fluorine) in electrophilic reactions of aromatic compounds, and of Allen *et al.*[15] concerning the "strong *para* directing influence of the fluorine substituent" (with fluoroindoles), are of interest in examining the results of nitration of fluorofluorenes (and 9-ones) and substituted fluorofluorenes. With only fluorine as a substituent, the unsubstituted ring is nitrated predominantly: 1-fluoro-, 2-fluoro-,[16] 3-fluoro-,[12] and 4-fluorofluorenone, and 2-fluorofluorene[17] all give the 7-nitro- derivative in high yield. When the non-fluoro-substituted ring is blocked with the 7-trifluoroacetamido- group (as above), nitration is mainly *ortho* to the 1-fluoro- substituent. However, 4-fluoro-7-trifluoroacetamidofluorene is nitrated *meta* to the fluorine in the 2-position (40%) and to a lesser extent (11%) in the 6-position. In reference[1] we assumed this was the 6-position, but in work described below, this is established beyond reasonable doubt: The known 7-acetamido-4-fluorofluorene was nitrated, presumably in the 6-position (2-acetamidofluorene is nitrated predominantly in the 3-(*ortho*)-position). Hydrolysis and trifluoroacetylation gave a substance identical with the 11% by-product above. In following papers in this series we expect to describe further directional effects in the nitration of fluorinated fluorene derivatives.

An attempt to confirm additionally the structure of the 2,1- isomer failed in its purpose, but gave interesting results. We diazotized 2-*N*,*N*-dimethylamino-1-fluorenamine[11] and carried out a Schiemann decomposition. The only product recovered (31%) was *N*-monomethyl-2-fluorenamine. It is possible that there was in the residual mixture a small amount of the desired 1-fluoro compound. A further instance of this type of monodemethylation is given in the next paper in this series.[12]

EXPERIMENTAL[18]

Improved procedure for N-2-(4-fluorofluorenyl)acetamide. 2-Fluoro-4-nitroiodobenzene. A slight molar excess of iodine monochloride (rather than with 3 molar equivalents[3]) was added dropwise at 80–82° (6 hr.) to *m*-nitroaniline. The reaction was kept at 80° for an additional 18 hr., yielding

---

(5) K. Inukai and Y. Maki, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **59**, 1162 (1956); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **78**, 1305 (1957).

(6) E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **21**, 1386 (1956).

(7) D. C. Morrison, *J. Org. Chem.*, **23**, 1772 (1958).

(8) H. A. Schoutissen, *J. Am. Chem. Soc.*, **55**, 4531 (1933).

(9) T. L. Fletcher and M. J. Namkung, *J. Org. Chem.*, **23**, 680 (1958).

(10) E. Sawicki and B. Chastain, *J. Org. Chem.*, **21**, 1028 (1956).

(11) M. J. Namkung and T. L. Fletcher, manuscript has been sent to this journal as Derivatives of Fluorene. VII.

(12) Work completed; manucript Fluorofluorenes. III to be submitted shortly.

(13) Dr. John H. Weisburger, National Cancer Institute, private communication and kind contribution of a copy of the infrared spectrum of his substance, m.p. 231–232° (see Experimental section).

(14) E. D. Bergmann, J. Blum, S. Butanaro, and A. Heller, *Tetrahedron Letters*, 15 (1959).

(15) F. L. Allen, P. Koch, and H. Suschitzky, *Tetrahedron*, 6, 315 (1959).

(16) Unpublished data, this laboratory.

(17) J. A. Miller, R. B. Sandin, E. C. Miller, and H. P. Rusch, *Cancer Research*, **15**, 188 (1955).

(18) Melting points were taken on a Fisher-Johns apparatus and are corrected to standards. Microanalyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were run (potassium bromide discs) on a Beckman IR-5 instrument.

39–46% of the iodo compound, m.p. 160–161° (lit.,[3] m.p. 160.5°), yellow needles. This was stirred (47 g., 0.18 mole) into 160 ml. of 48–50% fluoboric acid in an ice-salt bath and diazotized with 12.5 g. (0.18 mole) of sodium nitrite in 28 ml. of water at 0–5°. The diazonium salt was filtered, washed with cold 5% fluoboric acid, methanol, and ether, and dried giving 59.2 g. (92.5%). This was decomposed in 20 g. batches and mixed with two volumes of sand, by heating at a bath temperature of 167–170° under aspirator vacuum for 30 min. After extraction with benzene and evaporation, the solid was recrystallized from methanol (Darco), giving 20.7 g. (44%) of the fluoro compound, m.p. 125–127.5°. Recrystallization from methanol gave an analytical sample, m.p. 128.5–129.5°.

Anal. Calcd. for $C_6H_3FINO_2$: C, 27.00; H, 1.13; N, 5.25. Found: C, 26.74; H, 1.16; N, 5.43.

4-Fluoro-2-nitro-9-oxofluorene. Activated copper powder (see ref. 1, footnote[16]), 60 g., with 19.4 g. (0.073 mole) of the above iodo-compound and 0.15 mole of either ethyl or methyl *o*-bromobenzoate in an Ullmann condensation, followed by the general procedures described in the previous fluorofluorene paper, gave 43% (7.6 g.) of yellow needles, m.p. 195.5–196.5°. With the methyl ester, reaction temperatures of 215–220° were required, 15–20° higher than with the ethyl ester, to obtain the same yields. Crystallization from a benzene-methanol mixture gave an analytical sample, m.p. 196–197°.

Anal. Calcd. for $C_{13}H_6FNO_3$: C, 64.20; H, 2.49; N, 5.76. Found: C, 64.23; H, 2.58; N, 5.64.

4-Fluoro-9-oxo-2-fluorenamine. 2-Nitro-4-fluorofluorenone (0.95 g.) was mixed with stannous chloride dihydrate (4 g.), concd. hydrochloric acid (4 ml.), and 95% ethanol (3 ml.). The mixture was boiled with stirring for 15 min. then cooled to room temperature. The yellow precipitate was filtered, washed with 1% hydrochloric acid, and stirred in 2*N* sodium hydroxide (150 ml.). The amine was filtered, washed, and dried. Recrystallization from toluene gave dark purple needles, 0.8 g. (97%), m.p. 251–252°. One more crystallization gave an analytical sample, m.p. 251.5–252.5°.

Anal. Calcd. for $C_{13}H_8FNO$: C, 73.23; H, 3.78; N, 6.57; F, 8.91. Found: C, 73.48; H, 3.52; N, 6.39; F, 8.55.

4-Fluoro-2-fluorenamine. 2-Amino-4-fluorofluorenone (6.3 g., 0.03 mole) was mixed with 85% hydrazine hydrate (10.8 ml.) and sodium hydroxide (4.6 g.) dissolved in 2,2′-oxydiethanol (130 ml.). The mixture was refluxed at 178–180° (bath) for 2.5 hr. and at 210° (bath) for 3.5 hr., stirred into cold water, filtered, washed, and dried giving 5.3 g. (90%) of the crude product, m.p. 116–122°. One crystallization from benzene raised the melting point to 121–123.5°. There was no depression of the melting point when this was mixed with an authentic sample.[1]

2-Acetamido-4-fluorofluorene. Acetic anhydride (3 g.; 1.1 equivalents) was added to the crude product obtained above (5.3 g.) with rapid stirring. After thorough mixing, the solid mass was heated on a steam bath for 15 min. with frequent stirring, then dried in a desiccator under vacuum with moistened sodium hydroxide. Recrystallization from aqueous ethanol (Darco) gave 5.9 g. (93%); melting point and mixture melting point with authentic sample, 196–197.5°.

Improved procedure for N-2-(5-fluorofluorenyl)acetamide. 4-Fluorofluorenone. A mixture of 4-aminofluorenone (137 g., 0.7 mole), 48–50% fluoboric acid (420 ml.), and water (250 ml.) was warmed to effect solution, then cooled to 0–5°. Sodium nitrite (48.4 g.; 0.7 mole) in water (70 ml.) was added gradually. After further stirring (30 min.), the salt was filtered, washed with cold 5% fluoboric acid, methanol, and ether, and dried, giving 190–200 g. (93–98.5%).

(a) The diazonium fluoborate (42.7 g.) was mixed with three times its volume of dry sand and heated under reduced pressure (aspirator vacuum) at a bath temperature of 80–85° for 45 min. The mixture was extracted with acetone which was evaporated. The residue was recrystallized from methanol (Darco) giving 19.4 g. One crystallization from ethanol gave 16.7 g. melting at 159–161° (61% from the amine).

(b) The diazonium fluoborate (39.6 g.) was suspended in 1 l. of toluene which was heated slowly until evolution of gas commenced (internal temperature, 65°). The temperature was maintained at 60–65° until evolution of gas ceased. Then the reaction mixture was cautiously heated to boiling and the precipitate removed by filtration. The filtrate was treated with Darco and concentrated to obtain the product which was recrystallized from ethanol giving yellow needles (67% on the basis of the amine used), m.p. 161–162.5°.

Anal. Calcd. for $C_{13}H_7FO$: C, 78.78; H, 3.56; F, 9.59. Found C, 78.83; H, 3.44; F, 9.11.

Reduction of 4-fluorofluorenone. A mixture of 2 g. of 4-fluorofluorenone, 5 g. of red phosphorus, 6 ml. of 48–50% hydriodic acid and 50 ml. of acetic acid was refluxed 40 hr. and filtered hot. The filtrate was boiled almost to dryness and the resulting oil was extracted by boiling with petroleum ether (b.p. 30–60°). This was decanted and evaporated on the steam bath in a current of air. The residue amounted to 1.6 g. (86%), m.p. 38–39°. Recrystallization from cyclopentane (Darco) gave a substance identical with 4-fluorofluorene[1] (melting point and mixture melting point).

5-Fluoro-2-nitro-9-oxofluorene. The above ketone (16.6 g.) was slowly added with stirring to a mixture of glacial acetic acid (80 ml.) and fuming nitric acid (80 ml., d. 1.50) at 35°. Concentrated sulfuric acid (12 ml.) was then added slowly and the reaction temperature rose to 56°. After cooling to room temperature, the mixture was chilled in an ice bath. The yellow needles were filtered, washed with cold acetic acid, and dried giving 13.2 g. (65%), m.p. 211.5–213°.

Anal. Calcd. for $C_{13}H_6FNO_3$: C, 64.20; H, 2.49; N, 5.76. Found: C, 63.97; H, 2.26; N, 5.92.

5-Fluoro-9-oxo-2-fluorenamine. A mixture of 5-fluoro-2-nitrofluorenone (50 g., 0.205 mole), stannous chloride dihydrate (200 g.), concd. hydrochloric acid (200 ml.), and 95% ethanol (125 ml.) was heated cautiously until the initial evolution of gas subsided. The pasty mixture was then boiled with stirring for 20 min. and cooled to room temperature. The solids were filtered and treated with 2*N* sodium hydroxide. The amine, after crystallization from toluene, melted at 204–205°, yielding 90–97° (39–42 g.).

Anal. Calcd. for $C_{13}H_8FNO$: N, 6.57. Found: N, 6.55.

N-2-(5-Fluoro-9-oxofluorenyl)acetamide. Acetylation of the preceding compound gave a substance, m.p. 245–246°.

Anal. Calcd. for $C_{15}H_{10}FNO_2$: C, 70.58; H, 3.95; N, 5.49. Found: C, 70.55; H, 4.00; N, 5.68.

5-Fluoro-2-fluorenamine. (a) Wolff-Kishner (Huang-Minlon) reduction of 5-fluoro-9-oxo-2-fluorenamine gave an oil which was acetylated to give the known amide[1] (49% in two steps).

(b) A mixture of 5-fluoro-9-oxo-2-fluorenamine (10 g., 0.047 mole), red phosphorus (22 g.), 47% hydriodic acid (30 ml.) and glacial acetic acid (250 ml.) was refluxed for 24 hr. As much acetic acid as possible was then distilled off, avoiding decomposition, and the remainder was diluted with water. The solution was filtered from the phosphorus and made alkaline with ammonium hydroxide. The oily precipitate was filtered, washed with ice water, and dried over phosphorus pentoxide (9.8 g.). This was extracted several times with 200 ml. portions of boiling *n*-hexane. The extract was concentrated until an oil began to separate. Then the mixture was chilled in ice water and white needles (4.5 g., 48%) were collected, m.p. 85–87°. A mixture melting point with the authentic compound showed no depression.

N-2-(5-Fluorofluorenyl)acetamide. Acetylation of the solid with acetic anhydride and one crystallization from aqueous ethanol (Darco) gave 87% of the known compound.

N-2-(8-Fluorofluorenyl)acetamide. 8-Fluoro-2-nitrofluorene. Diazotization of 2-nitro-8-fluorenamine (25.2 g.) in 270 ml. of 48–50% fluoboric acid and 270 ml. of 85% phosphoric acid with 17 g. of sodium nitrite in 100 ml. of water, with subsequent stirring at 0–5° for 1.5 hr., gave the salt, which was recovered and dried in the usual way. This was slowly added to boiling toluene (400 ml.). The mixture was gently boiled an additional hour with occasional addition of boiling toluene. Filtration and evaporation of the toluene followed by crystallization from ethanol (Darco) gave 75–80% yields of the substance, m.p. 141–142°. Recrystallization from ethanol gave an analytical sample, m.p. 143–143.5°.

Anal. Calcd. for $C_{13}H_8FNO_2$: C, 68.12; H, 3.52; N, 6.11. Found: C, 68.22; H, 3.51; N, 6.17.

8-Fluoro-2-fluorenamine. A solution of 12.0 g. of the above nitro compound in 500 ml. of toluene and 500 ml. of ethanol was reduced with 12 ml. of hydrazine hydrate and Raney nickel in the usual way.[9] The snow-white product, 9.9 g. (95%), melted at 138–139.5°. Recrystallization from ligroin gave an analytical sample, m.p. 139–139.5° (slight softening at 138°).

Anal. Calcd. for $C_{13}H_{10}FN$: C, 78.37; H, 5.02; N, 7.03. Found: C, 78.63; H, 5.20; N, 7.01.

N-2-(8-Fluorofluorenyl)acetamide. To 10 g. of the amine in 50 ml. of benzene, 6 g. of acetic anhydride was added, and the mixture was warmed for 15 min. on the steam bath. The white precipitate was filtered and dried, 11.6 g., m.p. 189–190°. One crystallization from alcohol gave an analytical sample, m.p. 189–190°.

Anal. Calcd. for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81; F, 7.88. Found: C, 74.97; H, 5.05; N, 6.23; F, 7.72.

1-Fluorofluorenone. A mixture of 4 g. of 1-aminofluorenone, 22 ml. of fluoboric acid, and 4 ml. of water was heated to aid salt formation, then cooled to 0°, and 1.5 g. of sodium nitrite in 6 ml. of water was added in the usual way for 10 min. and stirred for an additional 20 min. Filtration, followed by washing, gave 6.0 g. (100%), dec. ~140°.

The diazonium salt was decomposed in 100 ml. of boiling xylene, replenishing this as evaporation proceeded. After 1 hr. no more acidic fumes were apparent and the mixture was filtered and boiled down to near dryness. The yield was 3.2 g. (78.5%), m.p. 107–110°. Recrystallization from ligroin (d. 0.67–0.69), with Darco treatment gave 2.9 g., m.p. 110–111.5°. An analytical sample was obtained after one recrystallization from alcohol.

Anal. Calcd. for $C_{13}H_7FO$: C, 78.78; H, 3.56; F, 9.59. Found: C, 79.05; H, 3.46; F, 9.34.

1-Fluoro-7-nitro-9-oxofluorene. To a mixture of 15 ml. of acetic acid and 15 ml. of fuming nitric acid (d. 1.5) 3 g. of 1-fluorofluorenone was added at 35°. All the solids dissolved and the solution became dark. Upon addition of 3 ml. of concd. sulfuric acid, the temperature rose to 50° and gradually cooled to room temperature. The mixture was diluted with water and the resulting light yellow precipitate filtered off, washed, and dried to give 3.65 g. (99%), m.p. 196–202°. Recrystallization from benzene gave a first crop, m.p. 210–211°, of 2.7 g. (74%). Another crystallization (ethanol) did not raise the melting point.

Anal. Calcd. for $C_{13}H_6FNO_3$: C, 64.20; H, 2.49; N, 5.76. Found: C, 64.12; H, 2.50; N, 6.08.

Oxidation of 1-fluoro-7-nitrofluorene. Sodium dichromate (3 g.) in glacial acetic acid was boiled for 10 min. with 1 g. of the compound. A near quantitative yield of product was recovered which, upon recrystallization from benzene (Darco), melted at 210–211°. A mixture melting point with the preceding compound showed no depression.

N-2-(8-Fluorofluorenyl)trifluoroacetamide. To a solution of 22.2 g. (0.072 mole) of 8-fluoro-2-fluorenamine in 200 ml. of hot benzene, a mixture of 20 g. (0.095 mole) of trifluoroacetic anhydride and 100 ml. of benzene was added slowly as a white precipitate formed. The mixture was boiled for 20 min. and cooled. A yield of 32.2 g. (98%) was obtained, m.p. 195–196°. One recrystallization from alcohol (Darco) gave an analytical sample, m.p. 195–195.5°.

Anal. Calcd. for $C_{15}H_9F_4NO$: N, 4.74. Found: N, 4.79.

N-2-(8-Fluoro-7-nitrofluorenyl)trifluoroacetamide. N-2-(8-Fluorofluorenyl)trifluoroacetamide (23 g.) was dissolved in 230 ml. of hot glacial acetic acid and cooled to 50°. Some precipitate formed. To the mixture, 23 ml. of nitric acid (d. 1.42) was added, while stirring and heating to 60°, at which point 3 ml. of concd. sulfuric acid was added with continuous thorough stirring. The solids dissolved, the temperature rose to 75° and a mass of yellow crystals formed. After cooling, the precipitate was filtered and washed with a little cold glacial acetic acid and then with alcohol and dried, giving 18.8 g. (71%), m.p. 242–245°. One recrystallization from toluene (Darco) gave an analytical sample 17.3 g., m.p. 245–245.5°.

Anal. Calcd. for $C_{15}H_8F_4N_2O_3$: N, 8.23. Found: N, 8.25.

By diluting the mother liquor with water, 5.6 g. of a second crop, m.p. 180–230° was obtained. This was recrystallized from alcohol and, in benzene solution, chromatographed through an alumina column, with benzene elution, giving 1.5 g. of *8-fluoro-7-nitro-2-fluorenamine*, m.p. 228–231°. A mixture melting point with the alkaline hydrolysis product (next paragraph) was not depressed.

8-Fluoro-7-nitro-2-fluorenamine. To a suspension of 12.3 g. (0.036 mole) of N-2-(8-fluoro-7-nitrofluorenyl)trifluoroacetamide in 1 l. of boiling alcohol, an aqueous solution (30 m.l) of sodium hydroxide (5 g.) was added with stirring. The solution turned dark red and the solid dissolved. Upon boiling for 5 min., a red precipitate formed. The boiling was continued for 10 more min. and the mixture cooled. After filtration, drying, and recrystallization from alcohol (Darco), 8.3 g. (94.5%), m.p. 230–231°, was recovered. One further recrystallization from alcohol gave an analytical sample, m.p. 231–231.5°.

Anal. Calcd. for $C_{13}H_9FN_2O_2$: C, 63.93; H, 3.72. Found: C, 63.97; H, 3.78.

1-Fluoro-2-nitrofluorene. To a mixture of 160 ml. of concd. hydrochloric acid and 2.4 g. (0.035 mole) of sodium nitrite in 20 ml. of water at 0°, 4.7 g. (0.019 mole) of 8-fluoro-7-nitro-2-fluorenamine was added in small portions with stirring, over a period of 10 min. The mixture was stirred for an additional hour at 0° and 160 ml. of precooled 50% hypophosphorous acid was added. Gas was given off, copiously at first. This mixture was stirred for 3 hr. and stored at 3° for 36 hr., then placed in a water bath at 40° for 2 hr. with stirring and again kept at 3° overnight. The light tan precipitate was filtered and dried, giving 4.3 g. (99%), m.p. 152–170°. Recrystallization from toluene (Darco) and sublimation yielded 2.6 g. (60%) of light yellow crystals, m.p. 179–180°. One recrystallization from toluene gave an analytical sample, m.p. 181–181.5°.

Anal. Calcd. for $C_{13}H_8FNO_2$: N, 6.11. Found: N, 6.12.

1-Fluoro-2-fluorenamine. 1-Fluoro-2-nitrofluorene (2.4 g.) was reduced in the usual way[9] giving 2.0 g. (96%) of the amine, m.p. 110–113°. One recrystallization from alcohol gave an analytical sample, m.p. 113–114°.

Anal. Calcd. for $C_{13}H_{10}FN$: N, 7.03. Found: N, 7.29.

N-2-(1-Fluorofluorenyl)acetamide. To a solution of 1.9 g. of 1-fluoro-2-fluorenamine in 30 ml. of toluene, 1 g. of acetic anhydride was added and the mixture was warmed on a steam bath for 10 min. and then boiled to near dryness. After blowing off the residual toluene, the precipitate was recrystallized from alcohol, giving 2.2 g. (96%), m.p. 181–182°. One further recrystallization gave an analytical sample, m.p. 182–183°. A mixture melting point with the alternate Ullmann product mentioned above[12] showed no depression.

Anal. Calcd. for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; F, 7.88; N, 5.81. Found: C, 74.86; H, 4.94; F, 7.84; N, 6.06.

1-Fluoro-2-nitrofluorenone. To a boiling solution of 1 g. of 1-fluoro-2-nitrofluorene in 30 ml. of glacial acetic acid, 3 g. of sodium dichromate (tech.) was added slowly with stirring. The mixture was boiled down to 5 ml., and 30 ml. of glacial acetic acid was added and then again it was boiled down to 5 ml. and cooled. The yellow precipitate was filtered and washed with 2 ml. of cold glacial acetic acid and with alcohol and dried, giving 0.8 g. (75.5%), m.p. 241–242°. One recrystallization from toluene (Darco) gave an analytical sample, m.p. 243.5–244°.

Anal. Calcd. for $C_{13}H_6FNO_3$: F, 7.81; N, 5.76. Found: F, 8.00; N, 5.85.

The infrared spectrum of this compound was identical with the spectrum mentioned above,[13] although our melting point is somewhat higher.

N-2-(5-Fluoro-3-nitrofluorenyl)acetamide (7-acetamido-4 fluoro-6-nitrofluorene). To a solution of 1 g. of *N*-2-(5-fluorofluorenyl)acetamide in 10 ml. of glacial acetic acid at 50°, 1 ml. of nitric acid (d. 1.42) was added with stirring. The mixture was heated to 55°, then removed from the heat. The temperature rose to 60° and a yellow precipitate formed. After cooling, filtration, and washing with 2 ml. of cold glacial acetic acid and water, the product was dried, giving 1.0 g. (84.5%), m.p. 240–246° dec. One recrystallization from alcohol (Darco) gave an analytical sample, m.p. 241–246° slow dec.

Anal. Calcd. for $C_{12}H_{11}FN_2O_3$: C, 62.90; H, 3.87; N, 9.79. Found: C, 63.03; H, 4.21; N, 10.00.

5-Fluoro-3-nitro-2-fluorenamine. Hydrolysis of the above compound in refluxing concd. hydrochloric acid-alcohol for 15 hr. gave a yield of 88% of the amine, m.p. 233–235°. One recrystallization from alcohol gave an analytical sample, m.p. 238–239°.

Anal. Calcd. for $C_{13}H_9FN_2O_2$: N, 11.47. Found· N, 11.34.

N-2-(5-Fluoro-3-nitrofluorenyl)trifluoroacetamide (7-trifluoroacetamido-4-fluoro-6-nitrofluorene). Acylation with trifluoroacetic anhydride in benzene solution gave a quantitative yield, m.p. 201.5–202.5°. A mixture melting point with the lesser (11%) product of nitration of 4-fluoro-7-trifluoroacetamidofluorene[1] was not depressed, 201.5–202.5°.

Diazotization and Schiemann decomposition of 2-N,N-dimethylamino-1-fluorenamine. A mixture of 5 g. of 2-dimethylamino-1-fluoroenamine, 38 ml. of 50% fluoboric acid, and 15 ml. of water was heated to effect solution then cooled in an ice-salt bath. To this, an aqueous solution (5 ml.) of 1.75 g. of sodium nitrite was added with stirring at 0°. The brick-colored diazonium salt was filtered, washed with 5% fluoboric acid, methanol, and then ether, and dried, giving 7.2 g. (80%), dec. 110°. The salt (7.2 g.) was heated in 140 ml. of benzene at the boiling point, and gradual decomposition took place. After 30 min. no more white fumes were apparent and a small amount of dark material had formed. Darco treatment of the filtrate was followed by evaporation to dryness. Ammonium hydroxide (10 ml.) was added and the white precipitate was extracted with 100 ml. of toluene in several portions, and the toluene solution was dried with a little anhydrous sodium sulfate and boiled down to near dryness. The precipitate was recrystallized from petroleum ether (b.p. 30–60°, Darco), giving 1.35 g. (31% based on the starting compound) of 2-methylaminofluorene, m.p. 77.5–78°. One recrystallization from cyclopentane raised the melting point to 78–78.5°. A mixture melting point with authentic 2-methylaminofluorene was not depressed. Acetylation of this product gave authentic *N*-methyl-*N*-2-fluorenylacetamide[19] (melting point and mixture melting point).

SEATTLE 5, WASH.

---

(19) T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Organophosphorus Chemistry. Addition Reactions of Diethyl Phosphonate and the Oxidation of Triethyl Phosphite[1]

M. S. KHARASCH,[2] ROBERT A. MOSHER,[3] AND IRVING S. BENGELSDORF[4]

Received October 1, 1959

The reactions of dialkyl phosphonates, with aldehydes and ketones to give dialkyl α-hydroxyalkylphosphonates, and with olefins to yield dialkyl alkylphosphonates are discussed. Trialkyl phosphites react smoothly and vigorously with hydroperoxides (oxidation-reduction) to yield the trialkyl phosphate and the corresponding alcohol. Cryoscopic molecular weight data reveal that the $\overset{+}{P}—\overset{-}{O}$ dipole readily enters into hydrogen-bonded associations with hydroxylic groups.

A series of stimulating lectures and discussions on newly discovered phosphorylation techniques[5] presented by Professor Alexander R. Todd in the autumn of 1948 led to the instant investigation of both heterolytic and homolytic reactions of phosphonic and phosphorous esters.[6]

Both chemical and physical evidence strongly support the existence of diethyl phosphonate as the keto structure (I) instead of the enol (II).[7]

$$\underset{\text{I}}{(C_2H_5O)_2P(O)H} \qquad \underset{\text{II}}{(C_2H_5O)_2\ddot{P}OH}$$

---

(1) Presented before the Symposium on Organophosphorus Chemistry at the 134th meeting of the American Chemical Society in Chicago, Illinois, September 1958.

(2) Deceased, October 1957. This paper is presented as a memorial tribute to the pioneering efforts in organophosphorus chemistry of the late Professor Kharasch.

(3) Present address: Standard Oil Research Department, Seymour, Indiana.

(4) Present address: TEXUS Research Center, Parsippany, New Jersey. To whom inquiries regarding this paper should be sent.

(5) (a) F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 382, 660 (1945); (b) F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 674 (1947).

(6) (a) The work presented in this paper was performed in the period 1948–1950; (b) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(7) The latest physical evidence still corroborates these conclusions. See infrared analyses by L. W. Daasch, *J. Am. Chem. Soc.*, **80**, 5301 (1958) and deuterium exchange studies by R. B. Fox and W. J. Bailey, Symposium on Organophosphorus Chemistry, 134th meeting of the American Chemical Society, Chicago, Illinois, September 1958, Abstracts, p. 70P.