82. *Organic Nitrates. Part II.* 9-Fluorenyl Nitrate.*

By G. W. H. Cheeseman.

The nitrate is converted into fluorenone by a variety of basic reagents and thus shows a marked tendency to undergo carbonyl elimination rather than to react by alkyl–oxygen fission.

9-Fluorenyl nitrate was prepared by reaction of equimolecular amounts of 9-chlorofluorene and silver nitrate in methyl cyanide. This reaction was considerably slower than that of 9-bromofluorene,[1, 2] but the chloro-compound was very readily prepared from fluoren-9-ol.[3] 9-Fluorenyl nitrate was comparatively stable at room temperature, whereas diphenylmethyl nitrate decomposed within a few hours at this temperature.[4] One batch of the nitrate did, however, decompose, with the evolution of brown fumes, after storage at room temperature for several months. Freeman [2] obtained fluoren-9-ol and fluorenone by thermal decomposition of the nitrate in chlorobenzene; fluorenone was also obtained when the nitrate was heated at 140° for 1 hr.

The reaction of 9-fluorenyl nitrate and aniline in the absence of solvent gave 9-anilinofluorene and aniline nitrate. When the reactants were dissolved in ether and the solution set aside at room temperature for 48 hr., the water-soluble nitrite formed indicated that a small percentage of α-hydrogen elimination had occurred, and unchanged nitrate was recovered from the ether-soluble products. When the nitrate was treated in methyl cyanide solution with benzylamine or morpholine, the yield of water-soluble nitrite was practically quantitative. Fluorenone was isolated from the ether-soluble products of the benzylamine reaction, and in the morpholine experiment the yield was nearly quantitative. A quantitative yield of fluorenone was also obtained on reaction of the nitrate with pyridine in methyl cyanide. Similarly fluorenone was formed exclusively when the nitrate was treated with methanolic potassium hydroxide.[2] From this work it was clear that 9-fluorenyl nitrate underwent carbonyl-elimination much more readily than diphenylmethyl nitrate. Baker and Heggs [5] studied the effects of structural changes on the carbonyl-elimination reactions of aralkyl nitrates, showing that carbonyl elimination was favoured by conjugation of a 1-phenyl substitutent with the forming double bond, also by factors which increase the strength of the nitric ester as a pseudo-acid. In the transition state for the formation of benzophenone both phenyl groups tend to conjugate with the forming carbonyl bond, but in the transition state for the formation of fluorenone a high degree of conjugation is possible between the forming double bond and the two coplanar *ortho*-linked phenyl groups. The pseudo-acidity of fluorene derivatives is well known. This is due to the peculiar stability of the *cyclo*pentadienyl-type anions resulting from the separation of a proton from position 9.[6]

When fluorenyl nitrate was heated with excess of acetamide, *N*-9-fluorenylacetamide was formed. Fluorenyl nitrate, however, failed to react with ethanol, thiophenol, sodium toluene-*p*-sulphinate, or 1 : 3 : 5-trimethoxybenzene under the mild conditions which led to reaction in the case of diphenylmethyl nitrate.[4] Thus, whereas diphenylmethyl nitrate underwent rapid solvolysis in ethanol at 20°, fluorenyl nitrate was recovered essentially unchanged after 72 hr. in solution in ethanol at room temperature. Rapid solvolysis did, however, occur at the boiling point of the solvent. Similarly, although diphenylmethyl

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* Part I, *J.*, 1957, 115. A preliminary account of some of the present work has appeared in *Chem. and Ind.*, 1956, 1390.

[1] Eaborn and Shaw, *J.*, 1955, 1420.
[2] Freeman, *J. Org. Chem.*, 1956, **21**, 471.
[3] Arcus and Mesley, *J.*, 1953, 180.
[4] Cheeseman, *J.*, 1957, 115.
[5] Baker and Heggs, *J.*, 1955, 616.
[6] Wilson Baker, " Perspectives in Organic Chemistry," Interscience Publ. Ltd., London, 1956, p. 37.

chloride is rapidly solvolysed in aqueous ethanol at 25°,[7] 9-chlorofluorene may be crystallised from this solvent. Fluorenyl nitrate did not react with thiophenol in methyl cyanide at room temperature. After 22 hr. at 56°, a mixture was obtained which on oxidation yielded some 9-fluorenyl phenyl sulphone. When a solution of the nitrate in thiophenol was set aside at room temperature, a vigorous reaction eventually took place. The products were separated chromatographically and diphenyl disulphide and fluorenone were isolated. Fluorenyl nitrate failed to react with sodium toluene-*p*-sulphinate in acetic acid or in boiling benzene; with ethanol as solvent a mixture of sulphone and 9-ethoxyfluorene was obtained. The decreased reactivity of fluorenyl nitrate compared with that of diphenylmethyl nitrate in these reactions, which are diagnostic of esters undergoing unimolecular alkyl–oxygen heterolysis,[8] indicated that the fluorenyl cation was the less readily formed. Conductivity measurements in sulphur dioxide at 0° show that 9-chloro-9-phenylfluorene has less tendency to ionise than has triphenylmethyl chloride.[9] It is suggested that the chloride shares in some of the resonance stabilisation of the 9-phenylfluorenyl anion whereas the cation does not. Conversely any factors which stabilise the cation would be expected to increase the degree of ionisation.

Freeman [2] observed that when 9-fluorenyl nitrate was dissolved in 95% sulphuric acid a deep blue-green colour appeared, and that fluoren-9-ol was formed when the solution was poured into water. When a drop of 72% perchloric acid was added to a solution of the nitrate in methyl cyanide an intense colour appeared. Anisole was added to this solution, but no 9-*p*-methoxyphenylfluorene was isolated from the mixture after 24 hr. at room temperature. The perchloric acid-catalysed reaction of fluoren-9-ol with anisole and phenol in nitromethane at 100° gave 9-*p*-methoxyphenylfluorene and 9-*p*-hydroxyphenylfluorene, respectively.

EXPERIMENTAL

Ethereal solutions were dried by azeotropic distillation with benzene. Nitrite was estimated colorimetrically.[10]

9-Fluorenyl Nitrate.—A mixture of 9-chlorofluorene (40·0 g., 0·20 mole) and silver nitrate (34·0 g., 0·20 mole) in methyl cyanide (150 ml.) was heated at 53° for 7 hr., then left overnight at room temperature. Silver chloride was filtered off and the filtrate evaporated in a vacuum. Extraction of the residue with light petroleum (b. p. 40—60°; 750 ml.) gave 9-fluorenyl nitrate as needles (27·3 g.), m. p. 86—89°. A further crop (9·5 g.), m. p. 80—85°, was obtained by concentration of the mother-liquor. The analytical specimen was crystallised from light petroleum (b. p. 40—60°; 15 parts) and had m. p. 88—89° (Found: C, 69·1; H, 4·0; N, 6·0. Calc. for $C_{13}H_9O_3N$: C, 68·7; H, 4·0; N, 6·2%). Eaborn and Shaw [1] give m. p. 89°. Extraction with glacial acetic acid of the light petroleum-insoluble material gave colourless needles of di-(9-fluorenyl) ether, m. p. 229—231°. The m. p. was raised to 231—232° by further crystallisation from glacial acetic acid (50 parts) (Found: C, 90·0; H, 5·5. Calc. for $C_{26}H_{18}O$: C, 90·1; H, 5·2%). Kleigl [11] gives m. p. 228°.

Decomposition of 9-Fluorenyl Nitrate.—The nitrate (1·15 g.) was heated at 140—150° for 1 hr. Water and ether were added, and the organic layer was separated, washed free from acid, dried, and evaporated. Crystallisation of the residue from 96% ethanol gave fluorenone (0·35 g.), m. p. and mixed m. p. 80—83°.

Reaction of 9-Fluorenyl Nitrate with Amines.—(a) *With aniline.* Heat was evolved when the nitrate (1·15 g.) and aniline (1·0 ml.) were mixed. After 2 hr., benzene was added and the crystalline precipitate of aniline nitrate (0·6 g.), m. p. 199—201° (decomp.), filtered off. The filtrate was evaporated in a vacuum and the residue (1·55 g.) shaken in ether with excess of 2N-hydrochloric acid. The hydrochloride which separated was filtered off and was

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[7] Ward, *J.*, 1927, 2285.

[8] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.

[9] Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience Publ. Ltd., London, 1956, p. 79.

[10] Barnes and Folkard, *Analyst*, 1951, **76**, 55.

[11] Kleigl, *Ber.*, 1910, **43**, 2488.

decomposed by treatment with ether and 2N-sodium hydroxide. The dried ethereal layer was evaporated in a vacuum. Crystallisation of the residual 9-anilinofluorene (0·92 g., 71%; m. p. 122—124°) from 96% ethanol (20 parts) gave needles, m. p. 123—124° (undepressed on admixture with an authentic sample [12]).

A mixture of the nitrate (3·4 g., 0·015 mole) and aniline (2·8 g.) in ether (30 ml.) was set aside for 2 days at room temperature, then poured into water. The ethereal layer was separated, and washed with water until the washings no longer gave a positive nitrite reaction, and then with 2N-hydrochloric acid. 9-Fluorenyl nitrate was recovered from the dried ethereal layer. The combined aqueous washings contained 0·00056 mole (4%) of nitrite.

(b) *With benzylamine.* When 9-fluorenyl nitrate (5·6 g., 0·025 mole) in methyl cyanide (20 ml.) was added to a solution of benzylamine (5·35 g., 0·05 mole) in methyl cyanide (10 ml.), heat was evolved. After 18 hr., water and ether were added, and the organic layer was separated and washed with water until the washings no longer gave a positive nitrite reaction. An unidentified yellow solid (0·2 g.), m. p. (mainly) 216—226°, separated slowly from the organic layer. This was collected and its m. p. was raised to 227—228° by two crystallisations from aqueous pyridine (Found: C, 88·8; H, 5·4; N, 5·5%). Evaporation of the dried filtrate and crystallisation of the residue from 96% ethanol gave fluorenone, m. p. and mixed m. p. 82—83° (oxime, m. p. and mixed m. p. 194—195°). The combined aqueous washings contained 0·023 mole (92%) of nitrite.

(c) *With morpholine.* When 9-fluorenyl nitrate (2·3 g., 0·01 mole) was added to a solution of morpholine (1·8 g.) in methyl cyanide (5 ml.) a vigorous reaction occurred. After 18 hr. the mixture was poured into water and ether, and the organic layer was separated and washed with water until the washings no longer gave a positive nitrite reaction. Evaporation of the dried ethereal layer gave fluorenone (1·76 g., 98%), m. p. and mixed m. p. 80—84°. The combined aqueous washings contained 0·010 mole (100%) of nitrite.

(d) *With pyridine.* Pyridine (1·6 ml.) was added to a solution of 9-fluorenyl nitrate (2·3 g.) in methyl cyanide (5 ml.). The mixture was then set aside at room temperature overnight. On dilution with water, nitrous fumes were evolved. The precipitate of fluorenone (1·8 g., 100%) had m. p. and mixed m. p. 82—84°.

Reaction of 9-*Fluorenyl Nitrate with Acetamide.*—A mixture of the nitrate (2·3 g.) and acetamide (2·4 g.) was heated at 100° for 30 min. Water was added and the residual oil solidified by trituration with 96% ethanol. The crystalline product (1·15 g., 52%), m. p. 249—255° (decomp.), gave colourless needles of *N*-9-fluorenylacetamide of unchanged m. p., on crystallisation from benzene (200 parts) or 96% ethanol (150 parts) (Found: C, 80·4; H, 6·0; N, 6·5. Calc. for $C_{15}H_{13}ON$: C, 80·7; H, 5·9; N, 6·3%). The amide is reported [13, 14] to have m. p. 246° and 262°.

Reaction of 9-*Fluorenyl Nitrate with Ethanol.*—The nitrate (1·15 g.) was heated under reflux with ethanol (10 ml.) for 30 min. and then cooled. Addition of water precipitated an oil which gradually solidified. The crude product (0·95 g., 90%) had m. p. *ca.* 40—50°. Successive crystallisations from aqueous ethanol gave colourless crystals of 9-ethoxyfluorene, m. p. 53—54° (Found: C, 85·7; H, 6·95. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%). Loevenich, Becker, and Schröder [15] give m. p. 54°.

Reaction of 9-*Fluorenyl Nitrate with Thiophenol.*—(*a*) A mixture of the nitrate (1·15 g.) and thiophenol (1·15 ml.) was set aside at room temperature. After some hours a vigorous reaction occurred. The product was isolated in ether and, after evaporation of solvent, the residue (1·85 g.) was dissolved in 1 : 10 benzene–light petroleum (b. p. 40—60°). The solution was filtered through a column of aluminium oxide (100 g.; Spence, type H, mesh 100—200), and the chromatogram developed with benzene–light petroleum (b. p. 40—60°) mixtures. A fraction (0·82 g.), m. p. 48—56°, eluted with 1 : 10 benzene–light petroleum, gave colourless needles of diphenyl disulphide (0·72 g.), m. p. and mixed m. p. 60—61° (from 96% ethanol). A fraction (0·20 g.), m. p. 69—73°, eluted with 1 : 1 benzene–light petroleum, gave fluorenone, m. p. and mixed m. p. 82—83° [from *cyclo*hexane–light petroleum (b. p. 40—60°)].

(*b*) A mixture of the nitrate (2·3 g.) and thiophenol (2·3 ml.) in methyl cyanide (5 ml.) was heated at 56° for 22 hr. After cooling, the crystalline precipitate (0·43 g.), m. p. 209—212°

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[12] Courtot and Petitcolas, *Compt. rend.*, 1925, **180**, 297.
[13] Langecker, *J. prakt. Chem.*, 1932, **132**, 145.
[14] Goldschmidt, *Annalen*, 1927, **456**, 152.
[15] Loevenich, Becker, and Schröder, *J. prakt. Chem.*, 1930, **127**, 248.

was filtered off. Crystallisation from acetic acid gave needles of di-(9-fluorenyl) ether, m. p. 225—227°. The original filtrate was diluted with water and ether, and the organic layer was separated, washed with water, dried, and evaporated. Crystallisation of the residue from benzene (5 ml.) and light petroleum (b. p. 40—60°; 5 ml.) gave impure fluoren-9-ol (0·45 g.), m. p. and mixed m. p. 139—142°. The mother-liquor was evaporated and the residue oxidised at room temperature with hydrogen peroxide (30% w/w; 5 ml.) in glacial acetic acid (50 ml.). After 18 hr., water was added and the crude product filtered off. Repeated crystallisations from 96% ethanol gave 9-*fluorenyl phenyl sulphone* as needles, m. p. 181—183° (Found: C, 74·0; H, 4·7; S, 11·0. $C_{19}H_{14}O_2S$ requires C, 74·5; H, 4·6; S, 10·5%).

Reaction of 9-*Fluorenyl Nitrate with Sodium Toluene*-p-*sulphinate*.—The nitrate (1·15 g.) was heated with sodium toluene-*p*-sulphinate (1·8 g.) in ethanol (20 ml.), under reflux for 45 min. After cooling, the precipitate was filtered off and extracted with water. The resulting 9-fluorenyl *p*-tolyl sulphone (0·5 g., 31%) had m. p. 225—227°. The m. p. was unchanged by crystallisation from butan-1-ol (20 parts) and was undepressed on admixture with an authentic sample.[16] Addition of water to the ethanolic mother-liquor precipitated 9-ethoxyfluorene (0·15 g.), m. p. 52—53·5°.

The nitrate failed to react with a suspension of powdered sodium toluene-*p*-sulphinate in boiling benzene.

9-p-*Hydroxyphenylfluorene*.—72% Perchloric acid (3 drops) was added to a solution of fluoren-9-ol (3·64 g.) and phenol (9·4 g.) in nitromethane (10 ml.). The mixture was kept at 100° for 3 hr., then cooled, and poured into water and ether. The organic layer was separated, washed free from acid, dried, and evaporated. Excess of phenol was removed in steam. Three crystallisations of the residue (4·6 g.), m. p. (mainly) 123—163°, from benzene, gave 9-*p*-hydroxyphenylfluorene as colourless needles, m. p. 182—183° (decomp.) (Found: C, 88·6; H, 5·7. Calc. for $C_{19}H_{14}O$: C, 88·35; H, 5·5%). Bistrzycki and von Weber [17] give m. p. 178—179° (decomp.).

9-p-*Methoxyphenylfluorene*.—72% Perchloric acid (3 drops) was added to a solution of fluoren-9-ol (3·64 g.) in anisole (12 ml.) and nitromethane (12 ml.). The mixture was kept at 100° for 3 hr., then cooled, and poured into water and ether. The organic layer was separated, washed free from acid, and dried. Solvent and excess of anisole were removed at 100°/20 mm. Crystallisation of the residue from ethanol gave colourless needles of 9-*p*-methoxyphenylfluorene (1·75 g., 32%), m. p. 117—120°. The m. p. was raised to 122—123° by further crystallisation from ethanol (10 parts) and light petroleum (b. p. 60—80°; 5 parts) (Found: C, 88·1; H, 6·2. Calc. for $C_{20}H_{16}O$: C, 88·2; H, 5·9%). Bistrzycki and von Weber [17] give m. p. 121—122°.

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QUEEN ELIZABETH COLLEGE, CAMPDEN HILL ROAD,
LONDON, W.8.

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[16] Ingold and Jessop, *J.*, 1930, 708.
[17] Bistrzycki and von Weber, *Ber.*, 1910, **43**, 2496.