83. *Organic Nitrates. Part III.* Triphenylmethyl Nitrate and 9-Phenyl-9-fluorenyl Nitrate.*

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Triphenylmethyl nitrate is extremely unstable and decomposes on attempted isolation. 9-Phenyl-9-fluorenyl nitrate is more stable, but is also hydrolysed in contact with air. The alkyl–oxygen bond in these compounds undergoes ready fission in a variety of reactions.

Experiments with diphenylmethyl nitrate[1a] suggested that triphenylmethyl nitrate would have versatile alkylating properties. In the case of the triphenylmethyl compound the possibility of concurrent α-hydrogen elimination reactions was structurally excluded.

Triphenylmethyl nitrate was prepared in ethereal solution from triphenylmethyl chloride and excess of powdered silver nitrate. Evaporation of the ethereal solution gave the solid nitrate which was converted into triphenylmethanol on short exposure to air.[1b] When the nitrate was heated with acetamide, *N*-triphenylmethylacetamide was formed in excellent yield. Merrow and Boschan[2] similarly alkylated hydrazine by reaction with the nitrate in ether. Interaction of ethereal solutions of triphenylmethyl nitrate and phenylmagnesium bromide gave some tetraphenylmethane.

As triphenylmethyl perchlorate was known to alkylate suitably activated aromatic compounds,[3] it was of interest to attempt to carry out similar reactions with triphenylmethyl nitrate. When a solution of triphenylmethyl chloride in anisole was added to one of silver nitrate in methyl cyanide, the subsequent reaction gave silver chloride, *N*-triphenylmethylacetamide, and a mixture of *o*- and *p*-nitroanisole, and may be represented by the following overall equation:

$$\mathrm{Ph_3C{\cdot}Cl + PhOMe + AgNO_3 + MeCN \longrightarrow Me{\cdot}CO{\cdot}NH{\cdot}CPh_3 + MeO{\cdot}C_6H_4{\cdot}NO_2 + AgCl}$$

Cristol and Leffler[4] have isolated a compound which they suggest may be the nitrate of the imidol form of *N*-triphenylmethylacetamide, from the reaction of a solution of triphenylmethyl chloride in methyl cyanide with one of silver nitrate in methyl cyanide:

$$\mathrm{Ph_3C{\cdot}Cl + AgNO_3 + MeCN \longrightarrow Me{\cdot}C(O{\cdot}NO_2){:}N{\cdot}CPh_3 + AgCl}$$

This substance was readily converted into *N*-triphenylmethylacetamide on crystallisation from commercial acetone or 96% ethanol. When *N*-triphenylmethylacetamide was formed in the system, triphenylmethyl chloride–anisole–silver nitrate–methyl cyanide, the bulk of the amide (80% of the total yield) crystallised directly from the reaction mixture. This suggests that imidol nitrate–anisole interaction may give *N*-triphenylmethylacetamide and nitroanisole. The parallel reactions between triphenylmethyl chloride dissolved in anisole, and silver nitrate dissolved in ethyl cyanide, phenyl cyanide, benzyl cyanide, and vinyl cyanide (acrylonitrile) were carried out, and the corresponding *N*-triphenylmethylamides isolated. A solution of silver nitrate in methyl cyanide underwent reaction with a 1 : 3-dimethoxybenzene solution of triphenylmethyl chloride to give *N*-triphenylmethylacetamide and a mixture of dimethoxynitrobenzenes, and with an anisole solution of *p*-methoxytriphenylmethyl chloride to give *N*-*p*-methoxytriphenylmethylacetamide.

Triphenylmethyl nitrate was extremely sensitive to hydrolysis: thus hydrolysis of the nitrate occurred when solutions of the nitrate in ether,[1a] benzene, or carbon tetrachloride[4] were exposed to air. The nitrate decomposed when heated under reflux in benzene[2] or toluene solution, oxides of nitrogen being evolved and triphenylmethanol formed. The

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* Part II, preceding paper.

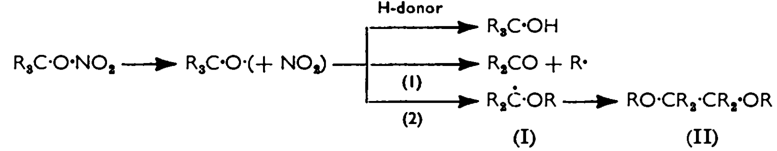
[1] Cheeseman, (*a*) *J.*, 1957, 115; (*b*) *Chem. and Ind.*, 1954, 281.

[2] Merrow and Boschan, *J. Amer. Chem. Soc.*, 1954, **76**, 4622.

[3] Burton and Cheeseman, *J.*, 1953, 832.

[4] Cristol and Leffler, *J. Amer. Chem. Soc.*, 1954, **76**, 4468.

decomposition of the nitrate presumably gives nitrogen dioxide and triphenylmethoxy-radicals which abstract hydrogen from a suitable donor to give triphenylmethanol. Cristol and Leffler[4] found that thermal decomposition of the nitrate in carbon tetrachloride or nitrobenzene gave triphenylmethanol, benzophenone, picric acid, and oxides of nitrogen. In order to explain the formation of benzophenone and picric acid they postulated β-cleavage of triphenylmethoxy-radicals (1) followed by a series of oxidation–reduction reactions to give picric acid:



Hawthorne[5] has prepared the more stable tri-*p*-nitrophenylmethyl nitrate and examined its thermal decomposition in chlorobenzene in the absence of air. This produced tri-*p*-nitrophenylmethanol, 4 : 4′-dinitrobenzophenone, 2 : 4-dinitrophenol, and the compound (II; $R = p\text{-}NO_2\cdot C_6H_4$), resulting from the Wieland rearrangement (2) of the tri-*p*-nitrophenylmethoxy-radical to the radical (I; $R = p\text{-}NO_2\cdot C_6H_4$), and subsequent dimerisation. An alternative path for the production of 4 : 4′-dinitrobenzophenone and 2 : 4-dinitrophenol involving the rearranged radical (I; $R = p\text{-}NO_2\cdot C_6H_4$) was also proposed.

In view of the difficulties in carrying out experiments with triphenylmethyl nitrate, 9-phenyl-9-fluorenyl nitrate was prepared. The structure of this tertiary nitrate was also such as to eliminate the possibility of both α- and β-hydrogen elimination. 9-Phenyl-9-fluorenyl nitrate was obtained by the action of excess of powdered silver nitrate on an ethereal solution of 9-chloro-9-phenylfluorene. The nitrate crystallised readily from ether–light petroleum mixtures and melted with decomposition at *ca.* 116—117°. The crystalline nitrate was hydrolysed (to 9-phenylfluoren-9-ol) on exposure to air, but less rapidly than triphenylmethyl nitrate. Heating the nitrate in an atmosphere of dry ammonia at 100° afforded di-(9-phenyl-9-fluorenyl) ether and 9-phenylfluoren-9-ol. Reaction of the nitrate with aniline and morpholine gave 9-anilino- and 9-morpholino-9-phenylfluorene, respectively. Treatment with excess of acetamide gave *N*-(9-phenyl-9-fluorenyl)acetamide; this compound was also obtained in high yield by heating a mixture of 9-phenylfluoren-9-ol and acetamide in the presence of a catalytic amount of concentrated sulphuric acid. The reaction of equimolecular amounts of the nitrate and toluene-*p*-sulphonamide in methyl cyanide gave a low yield of the expected sulphonamide. This was probably due to concurrent reaction of the nitrate with solvent, as a solution of the nitrate in methyl cyanide at room temperature soon became yellow and brown fumes were evolved. Addition of water precipitated high-melting solid of relatively high nitrogen content, indicating that nitration may have occurred. 9-Phenyl-9-fluorenyl nitrate underwent rapid solvolysis in methanol or ethanol at room temperature. Reaction with thiophenol, 1 : 3 : 5-trimethoxybenzene, and sodium toluene-*p*-sulphinate in ether at room temperature gave phenyl 9-phenyl-9-fluorenyl sulphide, 1 : 3 : 5-trimethoxy-2-(9-phenyl-9-fluorenyl)benzene, and 9-phenyl-9-fluorenyl *p*-tolyl sulphone, respectively. In these respects 9-phenyl-9-fluorenyl nitrate showed the typical reactivity of an ester undergoing unimolecular alkyl–oxygen heterolysis.[6]

EXPERIMENTAL

Ethereal solutions were dried by azeotropic distillation with benzene.

Reaction of Triphenylmethyl Nitrate with Acetamide.—Powdered silver nitrate (10 g.) was added to a solution of triphenylmethyl chloride (7·0 g.) in dry ether (50 ml.). The mixture was

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[5] Hawthorne, *J. Amer. Chem. Soc.*, 1955, **77**, 5521.
[6] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 362.

heated under reflux for 1 hr., then filtered in a closed system. The residual silver chloride weighed 3·59 g. (100%) after being washed with water. Acetamide (5·9 g.) was added to the ethereal filtrate, solvent was removed, and the residue heated at 80—120° for 1 hr. The mixture was then cooled and extracted with water, and *N*-triphenylmethylacetamide (6·95 g., 92%), m. p. (mainly) 204—210°, filtered off. Crystallisation from benzene (11 parts) gave the pure amide, m. p. 211—213° (undepressed on admixture with an authentic sample [7]).

Reaction of Triphenylmethyl Nitrate with Phenylmagnesium Bromide.—A solution of triphenylmethyl nitrate (from triphenylmethyl chloride, 7·0 g.) in ether (50 ml.) was added dropwise to one of phenylmagnesium bromide (prepared from magnesium, 1·25 g.). The mixture, from which solid had separated, was heated under reflux for 15 min., then cooled and decomposed with 2N-sulphuric acid. The organic layer was separated, washed free from acid, dried, and evaporated. Ether (25 ml.) was added to the residue, and the solid filtered off. Crystallisation from benzene gave tetraphenylmethane (0·2 g.) as needles, m. p. 274—277°. The m. p. was raised to 278—280° by further crystallisation from benzene (30 parts) and sublimation at 220—230°/1 mm. (Found: C, 93·8; H, 6·2. Calc. for $C_{25}H_{20}$: C, 93·7; H, 6·3%). Ullmann and Münzhuber [8] give m. p. 282°.

Reaction in the System, Triphenylmethyl Chloride–Anisole–Silver Nitrate–Methyl Cyanide.—Triphenylmethyl chloride (13·9 g., 0·05 mole) in anisole (21·6 g., 0·20 mole) was added dropwise to a water-cooled solution of silver nitrate (8·5 g., 0·05 mole) in methyl cyanide (25 ml.), so that the temperature did not exceed 20°. The mixture was set aside at room temperature for 3 days, and the solid obtained by filtration was extracted with benzene (Soxhlet). The residual silver chloride weighed 7·0 g. (97%) and the extract yielded *N*-triphenylmethylacetamide (9·9 g.), m. p. 212—213°. The m. p. was unchanged by crystallisation from ethanol (20 parts) and was undepressed on admixture with an authentic sample [7] (Found: C, 84·0; H, 6·5; N, 4·7. Calc. for $C_{21}H_{19}ON$: C, 83·7; H, 6·35; N, 4·7%). The original filtrate was poured into water and ether, and the organic layer separated, washed free from acid, dried and evaporated. Solvent and excess of anisole were removed by heating to 80°/1·5 mm. Crystallisation of the residue from benzene gave *N*-triphenylmethylacetamide (2·6 g.), m. p. 211—212°. The total yield was thus 83%. The mother-liquor was evaporated in a vacuum; distillation of the residue at 0·8 mm. gave a nitroanisole fraction (6·0 g., 78%), b. p. 101—105°. The analytical specimen had b. p. 92—93°/0·7 mm., n_D^{17} 1·571 (Found: C, 55·9; H, 5·0; N, 8·7. Calc. for $C_7H_7O_3N$: C, 54·9; H, 4·6; N, 9·15%).

Reaction in the System, Triphenylmethyl Chloride–Anisole–Silver Nitrate–Ethyl Cyanide.—Triphenylmethyl chloride (13·9 g.) in anisole (21·6 g.) was caused to react similarly with a solution of silver nitrate (8·5 g.) in ethyl cyanide (25 ml.). After 7 days at room temperature, the mixture was filtered and the solid extracted with benzene (Soxhlet). The extract gave N-*triphenylmethylpropionamide* (7·0 g., 44%), m. p. 193—194°. The m. p. was unchanged by further crystallisation from benzene (10 parts) (Found: C, 84·1; H, 6·7; N, 4·1. $C_{22}H_{21}ON$ requires C, 83·8; H, 6·7; N, 4·4%). The original filtrate was poured into ether and water. Distillation of the washed and dried organic layer yielded a nitroanisole fraction (3·8 g., 50%), b. p. 105—108°/1·5 mm., n_D^{21} 1·568. The residue gave impure triphenylmethanol, m. p. (mainly) 142—149°, on crystallisation from benzene.

Reaction in the System, Triphenylmethyl Chloride–Anisole–Silver Nitrate–Phenyl Cyanide.—Triphenylmethyl chloride (6·95 g.) in anisole (10·8 g.) was caused to react similarly with a solution of silver nitrate (4·25 g.) in phenyl cyanide (10 ml.). After 7 days at room temperature, the mixture was filtered, and the filtrate poured into ether and water. The washed and dried organic layer yielded a nitroanisole fraction (2·5 g., 65%), b. p. 98—110°/1·5 mm., n_D^{19} 1·570, on distillation. Crystallisation of the residue from ethanol gave *N*-triphenylmethylbenzamide (4·9 g., 54%), m. p. 160—163°. The pure amide, m. p. 163—164°, was obtained by successive crystallisation from ethanol (5 parts) and benzene–light petroleum (b. p. 40—60°) (1 : 2; 6 parts) (Found: C, 86·0; H, 6·1; N, 3·7. Calc. for $C_{26}H_{21}ON$: C, 85·9; H, 5·8; N, 3·9%). The m. p.s recorded [9, 10] for this compound are 160—162° and 165·5°.

Reaction in the System, Triphenylmethyl Chloride–Anisole–Silver Nitrate–Benzyl Cyanide.—Triphenylmethyl chloride (6·95 g.) in anisole (10·8 g.) was caused to react similarly with

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[7] Fosse, *Bull. Soc. chim. France*, **1931**, **49**, 159.
[8] Ullmann and Münzhuber, *Ber.*, 1903, **36**, 409.
[9] Vosburgh, *J. Amer. Chem. Soc.*, 1916, **38**, 2087.
[10] Brander, *Rec. Trav. chim.*, 1918, **37**, 78.

a solution of silver nitrate (4·25 g.) in benzyl cyanide (10 g.). After 7 days at room temperature, the mixture was filtered and the solid extracted with benzene (Soxhlet). The extract yielded N-(*triphenylmethyl*)*phenylacetamide* (6·2 g., 66%), m. p. (mainly) 186—188°. Successive crystallisation from benzene (5 parts) and ethanol (20 parts) gave the pure amide, m. p. 191—192° (Found: C, 86·0; H, 6·1; N, 3·6. $C_{27}H_{23}ON$ requires C, 85·9; H, 6·1; N, 3·7%).

Reaction in the System, Triphenylmethyl Chloride–Anisole–Silver Nitrate–Acrylonitrile.—Triphenylmethyl chloride (6·95 g.) in anisole (10·8 g.) was caused to react similarly with a solution of silver nitrate (4·25 g.) in acrylonitrile (10 ml.). After 7 days at room temperature, the mixture was filtered and the filtrate poured into ether and water. The organic layer was separated, washed with water, dried, and heated to 100°/20 mm. Ether was added to the residual oil, and, after cooling, the solid (1·0 g.), m. p. 185—192°, filtered off. Crystallisation from ethanol gave N-*triphenylmethylacrylamide* (0·6 g., 8%), m. p. 203—205°. The m. p. was raised to 204—206° by further crystallisation from ethanol (25 parts) (Found: C, 84·2; H, 6·3; N, 4·7. $C_{22}H_{19}ON$ requires C, 84·3; H, 6·1; N, 4·5%).

*Reaction in the System, Triphenylmethyl Chloride–*1 : 3-*Dimethoxybenzene–Silver Nitrate–Methyl Cyanide.*—Triphenylmethyl chloride (6·95 g.) in 1 : 3-dimethoxybenzene (13·8 g.) was caused to react similarly with a solution of silver nitrate (4·25 g.) in methyl cyanide (25 ml.). The mixture was set aside at room temperature for 2 days and then filtered. The solid was extracted with chloroform (Soxhlet). Evaporation of the extract gave *N*-triphenylmethylacetamide (1·85 g.), m. p. 211—213°. The filtrate was distilled in steam and *ca.* 2 l. of distillate collected. Crystallisation of the non-volatile solid from ethanol gave *N*-triphenylmethylacetamide (1·75 g.), m. p. (mainly) 208—210°. The total yield was thus 48%. The distillate deposited needles (1·0 g.) on cooling, which after two crystallisations from ethanol (10 parts) gave slightly impure 2 : 4-dimethoxy-1-nitrobenzene, m. p. 69—71° (Found: C, 52·9; H, 4·9; N, 7·45. Calc. for $C_8H_9O_4N$: C, 52·4; H, 4·95; N, 7·65%). 2 : 4-Dimethoxy-1-nitrobenzene is reported to have m. p.s ranging from 73° to 76—77°.

Reaction in the System, p-*Methoxytriphenylmethyl Chloride–Anisole–Silver Nitrate–Methyl Cyanide.*—*p*-Methoxytriphenylmethyl chloride (6·17 g., 0·02 mole) in anisole (12·9 g., 0·12 mole) was caused to react similarly with a solution of silver nitrate (3·4 g., 0·02 mole) in methyl cyanide (50 ml.). After 4 days at room temperature, the mixture was filtered and the filtrate distilled in steam. The non-volatile material (6·4 g.) was extracted with ether and N-(p-*methoxytriphenylmethyl*)*acetamide* (2·7 g., 41%), m. p. (mainly) 173—177° filtered off in two crops. The m. p. was raised to 180—181° by crystallisation from aqueous acetone (Found: C, 79·4; H, 6·4. $C_{22}H_{21}O_2N$ requires C, 79·7; H, 6·4%). Treatment of the ethereal mother-liquor with acetyl chloride gave *p*-methoxytriphenylmethyl chloride, m. p. 118—122° (undepressed on admixture with an authentic sample [11]). Chloroform extraction of the steam distillate and distillation of the dried extracts gave a nitroanisole fraction (0·6 g.), b. p. (mainly) 134°/2·2 mm., n_D^{22} 1·565.

Reaction in the System, Triphenylmethyl Chloride–Silver Nitrate–Methyl Cyanide.—Triphenylmethyl chloride (6·95 g.) was added to a solution of silver nitrate (4·25 g.) in methyl cyanide (25 ml.). After 7 days at room temperature, the mixture was filtered and the filtrate poured into ether and water. The residual silver chloride weighed 3·5 g. (98%). The organic layer was separated, washed free from acid, dried, and evaporated. Treatment of the residue with ether (50 ml.) gave *N*-triphenylmethylacetamide (0·7 g.), m. p. (mainly) 198—209°. The m. p. was raised to 209—212° by crystallisation from benzene and was undepressed on admixture with an authentic sample. Concentration of the ethereal mother-liquor gave triphenylmethanol, m. p. and mixed m. p. 160—162·5°.

9-*Phenyl*-9-*fluorenyl Nitrate.*—Powdered silver nitrate (1·7 g., 0·01 mole) was added to a solution of 9-chloro-9-phenylfluorene [12] (2·8 g., 0·01 mole) in dry ether (25 ml.), and the mixture heated under reflux for 1 hr. Silver nitrate (1·7 g.) was then added and heating continued for 1 hr. Silver salts were filtered off; the residual silver chloride weighed 1·45 g. (100%) after being washed with water. The filtrate was evaporated in a vacuum and ether (15 ml.) added to the residue. Small amounts of insoluble matter were removed, and the filtrate was diluted with light petroleum (b. p. 40—60°; 15 ml.). On refrigeration, colourless crystals of 9-*phenyl*-9-*fluorenyl nitrate* separated; a sample heated from 90° had m. p. *ca.* 116—117° (decomp.)

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[11] Burton and Cheeseman, *J.*, 1955, 3089.

[12] Hurd and Mold, *J. Org. Chem.*, 1948, **13**, 339.

(Found: C, 75·6; H, 4·3; N, 4·3. $C_{19}H_{13}O_3N$ requires C, 75·25; H, 4·3; N, 4·6%). Complete solvolysis showed 98% purity. The nitrate was stored at 0° in a desiccator (KOH). Complete solvolysis after 4 weeks showed 92% purity.

Decomposition of 9-*Phenyl*-9-*fluorenyl Nitrate*.—(a) *At room temperature*. The nitrate (1·05 g.) was left in a porcelain dish at room temperature for several days. 96% Ethanol (5 ml.) and water (1 ml.) were then added. After cooling, the crystalline precipitate of 9-phenylfluoren-9-ol (0·5 g.), m. p. 108—110° (undepressed on admixture with an authentic sample [13]), was filtered off.

(b) *In methyl cyanide*. A solution of the nitrate (0·91 g.) in methyl cyanide (10 ml.) became yellow at room temperature and nitrous fumes were evolved. After 18 hr., water was added, and the crystalline precipitate (0·7 g.), m. p. 219—222°, was filtered off. The m. p. was raised to 226—227° by successive crystallisation from ethanol (75 parts) and aqueous acetic acid (Found: C, 75·8; H, 5·1; N, 7·0%).

(c) *On heating in an atmosphere of ammonia*. A solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.) was evaporated in a stream of dry ammonia. The residue was then heated cautiously in an atmosphere of ammonia to 100°, and kept at 100° for 1 hr. 2N-Hydrochloric acid and chloroform were added, and the organic layer was separated, washed free from acid, dried, and evaporated. Crystallisation of the residue from methanol (5 ml.) gave di-(9-phenyl-9-fluorenyl) ether (0·6 g.), m. p. (mainly) 210—220°. Successive crystallisation from ethanol (200 parts) and *cyclo*hexane (20 parts) furnished crystals, m. p. 237—239° (undepressed on admixture with an authentic sample [14]) (Found: C, 91·2; H, 5·6. Calc. for $C_{38}H_{26}O$: C, 91·2; H, 5·3%). The methanolic mother-liquor was evaporated and the residue extracted with light petroleum (b. p. 60—80°; 100 ml.). The extract slowly deposited crystals of 9-phenylfluoren-9-ol, m. p. 107—109°.

A sample of the nitrate heated at 120° for 30 min. decomposed to give an oil from which no crystalline material was isolated.

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Aniline*.—Aniline (1·86 ml.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). The mixture was left at room temperature overnight, then poured into water. The organic layer was separated, washed successively with water, 2N-sodium hydroxide, and water, dried, and evaporated. Methanol (10 ml.) was added to the residue, and the precipitate of 9-anilino-9-phenylfluorene (1·8 g., 54%), m. p. (mainly) 173—175°, filtered off. The m. p. was raised to 178—180° by two crystallisations from butan-1-ol (10 parts), and was undepressed on admixture with an authentic sample.[15]

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Morpholine*.—Morpholine (2 ml.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). The mixture was left at room temperature overnight and then solvent was removed. Water was added to the residue, and the product filtered off. Crystallisation from butan-1-ol gave 9-*morpholino*-9-*phenylfluorene* (1·8 g., 55%), m. p. 228—230°. The m. p. was raised to 233—234° by crystallisation from either light petroleum (b. p. 80—100°; 60 parts) or butan-1-ol (20 parts) (Found: C, 84·0; H, 6·7; N, 4·3. $C_{23}H_{21}ON$ requires C, 84·4; H, 6·5; N, 4·3%).

In another experiment, a reaction mixture of similar composition was left at room temperature overnight and then poured into water. The organic layer was separated, washed with water, dried, and evaporated, and the residue dissolved in methanol (5 ml.). On dilution with a little water, an oil was precipitated which gradually solidified. After several crystallisations of the crude product (1·2 g.), m. p. (mainly) 77—87°, from 96% ethanol, 9-methoxy-9-phenylfluorene, m. p. 94—95°, was obtained (Found: C, 88·0; H, 6·2. Calc. for $C_{20}H_{16}O$: C, 88·2; H, 5·9%). Kleigl [15] gives m. p. 92·5—93°. The aqueous-methanolic mother-liquor yielded a fraction (0·3 g.) of m. p. (mainly) 210—225°. Crystallisation from light petroleum (b. p. 60—80°) gave 9-morpholino-9-phenylfluorene, m. p. 230—232°. Evaporation of the combined aqueous washings gave a crystalline residue, which yielded morpholine nitrate, m. p. 140—142° (undepressed on admixture with an authentic sample [1a]), on recrystallisation from ethanol.

9-Morpholino-9-phenylfluorene was also obtained by heating a mixture of 9-chloro-9-phenylfluorene (2·8 g.) and morpholine (10 ml.) at 95° for 2 hr. Water was then added and the

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[13] Ullmann and von Wurstemberger, *Ber.*, 1904, **37**, 73.

[14] Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 200.

[15] Kleigl, *Ber.*, 1905, **38**, 284.

precipitate filtered off. Crystallisation from light petroleum (b. p. 80—100°) gave the pure morpholino-compound (2·6 g., 80%), m. p. 232—234°.

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Acetamide.*—Acetamide (3·0 g.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). Solvent was removed and the residue heated at 80—100° for 1 hr. The mixture was then extracted with water, and the product (3·0 g.), m. p. (mainly) 220—225°, filtered off. Crystallisation from benzene (50 parts) gave *N*-(9-phenyl-9-fluorenyl)acetamide (2·1 g., 70%), m. p. 228—230°. The m. p. was unchanged by further crystallisation from ethanol (40 parts) (Found: C, 84·1; H, 5·8; N, 4·4. Calc. for $C_{21}H_{17}ON$: C, 84·2; H, 5·7; N, 4·7%). Pinck and Hilbert [16] give m. p. 232°.

The amide was also obtained by heating 9-phenylfluoren-9-ol (3·0 g.), acetamide (3·0 g.) and concentrated sulphuric acid (5 drops) at 210—220° for 45 min. After cooling, the mixture was extracted with water, and the product (3·5 g.), m. p. (mainly) 223—227°, filtered off. Crystallisation from butan-1-ol (12 parts) gave the amide (2·8 g., 81%), m. p. 228—231°.

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Toluene*-p-*sulphonamide.*—A mixture of the nitrate (1·52 g.) and toluene-*p*-sulphonamide (0·85 g.) in methyl cyanide (10 ml.) was set aside at room temperature overnight. Water was added, and, after refrigeration, the precipitate filtered off and dissolved in hot 96% ethanol (40 ml.). The solution was allowed to cool to room temperature, then filtered. The filtrate deposited crystals of N-(9-*phenyl*-9-*fluorenyl*)-*toluene*-p-*sulphonamide* (0·25 g., 12%), m. p. (mainly) 188—192°. The m. p. was raised to 193—194° by two further crystallisations from 96% ethanol (100 parts) (Found: C, 75·9; H, 5·5; N, 3·2; S, 7·5. $C_{26}H_{21}O_2NS$ requires C, 75·6; H, 5·15; N, 3·4; S, 7·8%).

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Ethanol.*—A mixture of the nitrate (0·61 g.) and ethanol (10 ml.) was set aside at room temperature overnight. Water was then added and the precipitate of 9-ethoxy-9-phenylfluorene (0·56 g., 97%), m. p. (mainly) 113—114°, filtered off. Crystallisation from 96% ethanol (20 parts) gave the pure ethoxy-compound, m. p. 114—115° (undepressed on admixture with an authentic sample [15]) (Found: C, 88·2; H, 6·5. Calc. for $C_{21}H_{18}O$: C, 88·0; H, 6·3%).

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Thiophenol.*—Thiophenol (1·1 ml.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). After 18 hr., solvent was removed. The crystalline residue (2·2 g., 65%) had m. p. (mainly) 116—119°, after washing with a little ether. Crystallisation from 96% ethanol (25 parts) gave *phenyl* 9-*phenyl*-9-*fluorenyl sulphide*, m. p. 118—120° (Found: C, 85·2; H, 5·3; S, 9·1. $C_{25}H_{18}S$ requires C, 85·7; H, 5·2; S, 9·15%).

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with* 1 : 3 : 5-*Trimethoxybenzene.*—1 : 3 : 5-Trimethoxybenzene (1·7 g.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). After 18 hr., the mixture was poured into excess of sodium hydrogen carbonate solution. The organic layer was separated. washed with water, dried, and evaporated. 96% Ethanol (10 ml.) was added to the residue, and the crystalline precipitate filtered off. Crystallisation from 96% ethanol gave 1 : 3 : 5-*trimethoxy*-2-(9-*phenyl*-9-*fluorenyl*)-*benzene* (2·4 g., 59%), m. p. 165—167°. The m. p. was unchanged by further crystallisation from 96% ethanol (50 parts) and light petroleum (b. p. 60—80°; 40 parts) (Found: C, 82·2; H, 6·1. $C_{28}H_{24}O_3$ requires C, 82·3; H, 5·9%).

The trimethoxy-compound was also prepared by adding 72% perchloric acid (2 drops) to a solution of 9-phenylfluoren-9-ol (2·6 g.) and 1 : 3 : 5-trimethoxybenzene (1·7 g.) in nitromethane (10 ml.). The mixture was left at room temperature overnight and then filtered. Crystallisation of the product from 96% ethanol gave 1 : 3 : 5-trimethoxy-2-(9-phenyl-9-fluorenyl)-benzene (3·2 g., 78%), m. p. 164—166°. This compound apparently crystallised in a low-melting form, m. p. 149—152°, from benzene–light petroleum (b. p. 40—60°) (1 : 1; 6 parts).

Reaction of 9-*Phenyl*-9-*fluorenyl Nitrate with Sodium Toluene*-p-*sulphinate.*—Powdered sodium toluene-*p*-sulphinate (2·7 g.) was added to a solution of the nitrate (from 9-chloro-9-phenylfluorene, 2·8 g.) in ether (25 ml.). The reaction mixture was heated under reflux for 1 hr., then left at room temperature for 3 days. Solvent was removed and water added to the residue. The sticky solid was filtered off and washed with ether. The ethereal layer was separated from the combined filtrate and washings, washed successively with water, sodium hydrogen carbonate solution, and water, dried, and evaporated. Methanol (5 ml.) was added to the residue and the solid filtered off. The total yield of 9-phenyl-9-fluorenyl *p*-tolyl sulphone

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[16] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1937, **59**, 8.

was thus 0·70 g. (19%), m. p. (mainly) 209—210°. The m. p. was raised to 211—212° by crystallisation from ethanol (70 parts) and was undepressed on admixture with an authentic sample.[17] 9-Methoxy-9-phenylfluorene, m. p. 93—94°, was isolated from the methanolic mother-liquor, indicating that the nitrate had only partly reacted.

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[*Received, August 25th,* 1958.]

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[17] Bassey, Buncel, and Davies, *J.*, 1955, 2550.