299. *Reactions of Organic Azides. Part V.* The Schmidt Reaction with Fluorenones. The Structure of the Intermediate in the Ketonic Schmidt Reaction.*

By C. L. ARCUS, M. M. COOMBS, and J. V. EVANS.

The conversion of substituted fluorenones into phenanthridones, by means of the Schmidt reaction, is described. There is no simple correlation between the electronic character, or bulk, of a phenylene ring in a fluorenone, and its migratory aptitude. The data now available in the literature provide numerous exceptions to Smith's suggested rule [1,2,3] that, in the Schmidt reaction with an unsymmetrical ketone, the group having the larger bulk in the neighbourhood of the keto-carbon atom migrates preferentially.

It is shown that Smith's mechanism, which involves dehydration and re-hydration of reaction intermediates, is improbable. An intermediate containing a hydrogen-bonded ring is suggested.

THE reaction of 2- and 3-substituted fluoren-9-ols with hydrazoic and sulphuric acids, to yield mixtures of the corresponding 2- and 7- or 3- and 6-substituted phenanthridines, is described in Part III.[4] The conversion, by the Schmidt reaction, of three monosubstituted fluorenones into pairs of isomeric phenanthridones is now reported.

Walls [5] was unable to isolate a pure product from the reaction of sodium azide with a solution of 2-methoxyfluorenone in sulphuric acid. By the addition of this fluorenone to a solution of hydrazoic acid in chloroform together with sulphuric acid, there has now been

---

* Part IV, *J.*, 1955, 1634.

[1] Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 320.

[2] Smith and Ashby, *ibid.*, 1950, **72**, 2503.

[3] Smith and Horwitz, *ibid.*, p. 3718.

[4] Arcus and Coombs, *J.*, 1954, 4319.

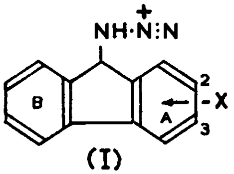
[5] Walls, *J.*, 1935, 1405.

obtained a mixture of 2- and 7-methoxyphenanthridone in 36% yield. In order to separate the isomers, the mixture was converted by phosphorus oxychloride into the corresponding 9-chlorophenanthridines; the yield was almost quantitative, whence the ratio of 9-chloro-2-methoxy- to 9-chloro-7-methoxy-phenanthridine in the product must be nearly the same as that of the two methoxyphenanthridones in the original mixture. Fractional crystallisation yielded these chloromethoxyphenanthridines in substantially equal amounts, whence it is concluded that the ratio of 2- to 7-methoxyphenanthridone in the original reaction product was approximately 1 : 1.

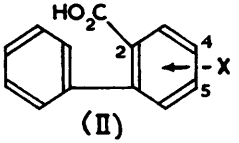
It is stated [6] that 2-nitrophenanthridone is the sole product when a solution of 2-nitrofluorenone in sulphuric acid is allowed to react with a solution of hydrazoic acid in benzene. By the addition of sodium azide to a solution of 2-nitrofluorenone in sulphuric acid, Walls [5] obtained a mixture of nitrophenanthridones which on reduction gave a mixture of aminophenanthridones which he considered identical with that obtained from the Schmidt reaction with 2-aminofluorenone; the latter mixture was converted, *via* diazotisation, into a mixture of 2- and 7-hydroxyphenanthridones which he separated into its components. Repetition of the reaction by Walls's method gave a high yield of nitrophenanthridones. Fractional vacuum-sublimation of the product yielded a small quantity of a relatively volatile material approximating in m. p. to that of the 1 : 2-complex of 2- and 7-nitrophenanthridone reported by Nunn, Schofield, and Theobald,[7] and less volatile fractions consisting substantially of 2-nitrophenanthridone, which they yielded on one recrystallisation. From the weights of the fractions, 2- and 7-nitrophenanthridone are concluded to have been formed in the ratio 19 : 1.

The Schmidt reaction (as for the 2-isomer) with 3-nitrofluorenone gave a high yield of nitrophenanthridones, fractional vacuum-sublimation of which gave a least-volatile fraction yielding, on one recrystallisation, 3-nitrophenanthridone. By the use of authentic specimens of the isomers, a m. p.–composition curve was constructed, and by its use 3- and 6-nitrophenanthridone were found to have been formed in the ratio 69 : 31.

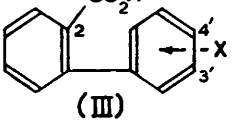
Mechanism of the Ketonic Schmidt Reaction.—Difference from the alcohol–olefin reaction. The migration ratios found for the phenanthridones formed from the three monosubstituted fluorenones, above, differ markedly from those relating to the similarly substituted phenanthridines derived from the corresponding fluoren-9-ols, respectively 32 : 68; 3 : 97; 6 : 94 (Part III [4]). The relative rates with which the substituted and unsubstituted rings migrate during the rearrangement of the protonated azide (whether derived from fluorenol or fluorenone) is directly given by the ratio of the yields of the corresponding phenanthridines (or phenanthridones). It is shown, qualitatively, in Part III,[4] that the ratios of the yields of isomeric phenanthridines are directly related to the capacities of the rings for electron-release at their point of attachment to $C_{(9)}$. It has been found possible to give this correlation a quantitative form, and to indicate the extent to which rates of migration of rings in the Schmidt reaction of the fluorenones are not correlated with electron-release.



(I)



(II)



(III)

In the rearrangement of the protonated azide (I), derived from a 2- (or 3-) substituted fluoren-9-ol, the rate of migration of ring A is dependent on the electron-availability at the point of attachment of A to $C_{(9)}$, and a measure of the " permanent " (*I* and *M*) part of this availability is given by the p*K* value of the corresponding 4- or 5-substituted diphenyl-2-carboxylic acid (II). Similarly, the electron-density at the point of attachment of B to $C_{(9)}$, which governs the rate of migration of ring B, is given by the p*K* value of the corresponding 3'- or 4'-substituted diphenyl-2-carboxylic acid (III).

[6] B.P. 333,173.

[7] Nunn, Schofield, and Theobald, *J.*, 1952, 2797.

On adapting the Hammett relation to a diphenyl system, and writing the rates of migration of A and B as k_A, k_B, and that of the unsubstituted phenylene ring [as in (I) with $X = H$] as k_H, and the pK values of the appropriate diphenyl-2-carboxylic acids as pK_A, pK_B, pK_H, we have :

$$\log (k_A/k_H) = r(\mathrm{p}K_A - \mathrm{p}K_H)$$

and

$$\log (k_B/k_H) = r(\mathrm{p}K_B - \mathrm{p}K_H)$$

where r is a constant, whence

$$\log (k_A/k_B) = r(\mathrm{p}K_A - \mathrm{p}K_B)$$

The ratio of the rate constants is the same as the ratio in which the products are formed, since the latter arise from a common precursor (I), whence :

$$\log \left[\frac{\%\text{ of product from migration of A}}{\%\text{ of product from migration of B}}\right] = r(\mathrm{p}K_A - \mathrm{p}K_B)$$

No dissociation constants are available for diphenyl-2-carboxylic acids except that for the unsubstituted acid.[8] However, Berliner and Blommers[9] have shown that the pK values for diphenyl-4-carboxylic acids, substituted in positions 3′ and 4′, and those for benzoic acids similarly substituted in the *meta*- and the *para*-position, are related by equation (1) having $a = 0\cdot37$:

$$\mathrm{p}K_{X2} - \mathrm{p}K_{Y2} = a(\mathrm{p}K_{X1} - \mathrm{p}K_{Y1}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where X2 denotes diphenyl-4-carboxylic acid with substituent X, X1 denotes benzoic acid with the corresponding substituent, Y2 denotes diphenyl-4-carboxylic acid with substituent Y, and Y1 denotes benzoic acid with the corresponding substituent.

In order to estimate values for the substituted diphenyl-2-carboxylic acids, two assumptions have been made: that the strength of diphenyl-2-carboxylic acid is influenced by substituents in the 3′- and 4′-positions to the same extent as is that of the 4-carboxylic acid; and that substituents in positions 4 and 5 influence the strength of diphenyl-2-carboxylic acid to the same extent as they do that of benzoic acid. Then, taking $Y = H$ in (1), and inserting $\mathrm{p}K_{Y2} = \mathrm{p}K$ $(3\cdot4597)$ for diphenyl-2-carboxylic acid,[8] and $\mathrm{p}K_{Y1} = \mathrm{p}K$ $(4\cdot2027)$ for benzoic acid,[10] $\mathrm{p}K_{X2}$ can be evaluated for 4-, 5-, 3′-, and 4′-substituted diphenyl-2-carboxylic acids by inserting the values of $\mathrm{p}K_{X1}$ appropriate to the corresponding *meta*- and *para*-substituted benzoic acids[10] and employing the values $a = 1\cdot00$ for 4- and 5-substituted and $a = 0\cdot37$ for 3′- and 4′-substituted diphenyl-2-carboxylic acids. By this means the following pK values have been estimated.

Diphenyl-2-carboxylic acid	4-NO_2	5-NO_2	4-Me	5-Me	4-MeO
pK	2·751	2·682	3·529	3·630	3·345

Diphenyl-2-carboxylic acid	3′-NO_2	4′-NO_2	3′-Me	4′-Me	4′-MeO
pK	3·197	3·172	3·485	3·523	3·559

In the Figure, for the reactions of five 2- or 3-substituted fluoren-9-ols reported in Part III[4] and for the three fluorenones above, the logarithms of the product ratios have been plotted against the differences in the pK values for the corresponding diphenyl-2-carboxylic acids. The points relating to the fluorenols lie near a straight line to an extent which is considered, in view of the assumptions which have been made, to be adequate to establish a direct correlation between the rate of migration of a ring and the electron-density at its point of attachment to $C_{(9)}$. No such correlation is apparent for the points relating to the fluorenones.

The mechanism by which, it is considered, fluoren-9-ols react with hydrazoic and sulphuric acids is set out in Parts I,[11] III,[4] IV.[12] Essentially similar mechanisms are

---

[8] Dippy and Lewis, *J.*, 1937, 1426.

[9] Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479.

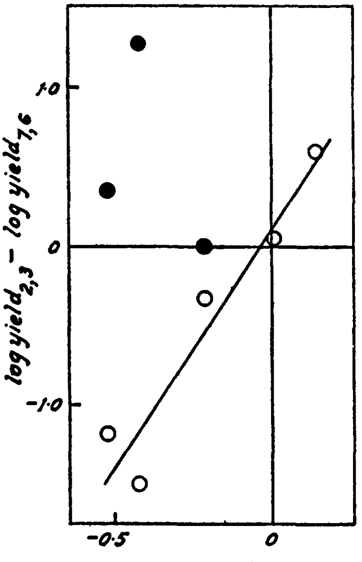
[10] Dippy, *Chem. Rev.*, 1939, **25**, 151.

[11] Arcus and Mesley, *J.*, 1953, 178.

[12] Arcus and Lucken, *J.*, 1955, 1634.

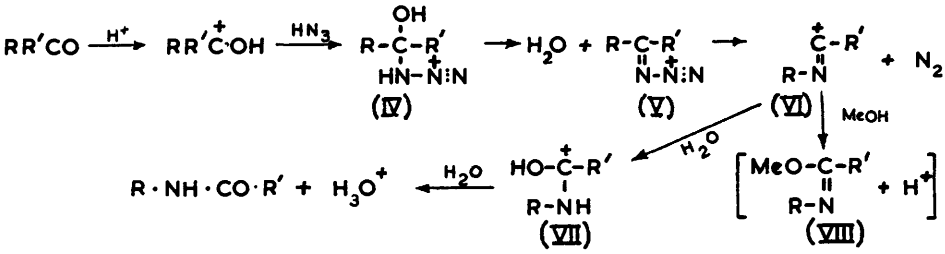
applicable to the reaction of 1 : 1-diarylethylenes with these reagents,[13] and the acid-catalysed decomposition of diarylazidomethanes [14] and of 1 : 1-diarylazidoethanes; [15] in each instance the respective authors have found that the migratory aptitude of a given group is directly related to its capacity for electron-release.

The results, reported above, on the Schmidt reaction with fluorenones add to the evidence [2,3,16] that the correlation between capacity for electron-release and migratory aptitude does not apply to the groups adjacent to the carbonyl group of a ketone which is undergoing the Schmidt reaction. It is concluded that there is a definite difference between the mechanism of the reaction of an alcohol or olefin with hydrazoic acid (in the presence of a strong acid), and that of a ketone with these reagents.



*Relation of yields of isomeric phenanthridines, and phenanthridones, from the reaction of fluoren-*9*-ols* (○), *and fluorenones* (●), *with hydrazoic and sulphuric acids, to values of* pK *of the corresponding diphenyl-*2*-carboxylic acids.*

The Structure of the Intermediate in the Ketonic Schmidt Reaction.—Smith [1,2,3] concluded from the available data that, in the Schmidt reaction with an unsymmetrical ketone, the group which has the larger bulk in the immediate neighbourhood of the keto-carbon atom usually migrates preferentially, and he proposed the following mechanism, which accommodates this finding:



The protonated azide (IV) loses water to give an oxime-like intermediate (V), which then undergoes a rearrangement analogous to the Beckmann rearrangement; (V) may be formed in either of two geometrically isomeric configurations, whence it is possible for the

---

[13] McEwen and Mehta, *J. Amer. Chem. Soc.*, 1952, **74**, 526.
[14] Tietz and McEwen, *ibid.*, 1955, **77**, 4007.
[15] Ege and Sherk, *ibid.*, 1953, **75**, 354.
[16] Westland and McEwen, *ibid.*, 1952, **74**, 6141.

isomer having the larger group *anti* to the N_2^+ group to be formed preferentially; rearrangement of this form leads to migration of the larger group. Hydration of the product from the last stage yields the protonated amide (VII).

An examination of the results of Schmidt reactions with unsymmetrical ketones, many reported since Smith's mechanism was proposed, shows that there are numerous exceptions to the rule that the group having the greater bulk in the vicinity of the carbonyl group migrates preferentially.

The evidence on electronic effects in the ketonic Schmidt reaction, referred to above, is derived from the reactions of *p*- and *pp'*-substituted benzophenones. The aryl groups of these ketones have essentially the same bulk in the neighbourhood of the carbonyl group, and this is substantially true of the two rings of the fluorenones, the Schmidt reactions of which are described above. The migratory aptitudes of rings in these compounds might therefore be expected to be unaffected by the presence of substituents. The aryl groups of the benzophenones migrated at about the same rate, except for *p*-methoxyphenyl, which migrated at twice the speed of phenyl in 4-methoxybenzophenone, but at nearly the same rate as 4-nitro- and 4-chloro-phenyl in 4-methoxy-4'-nitro- and 4-chloro-4'-methoxy-benzophenone. In fluorenone the presence of a 2-methoxy-group did not affect the migratory aptitude of the substituted ring, which was increased by a 3-nitro- and markedly by a 2-nitro-substituent.

The following data have been recorded concerning ketones which are not symmetrical in the immediate vicinity of the carbonyl group. Smith and Horwitz [3] found, for a series of alkyl phenyl ketones, that the relative extent of migration of the alkyl group increases in the order $\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^i < \mathrm{Bu}^t$ (the course of the reaction with *tert.*-butyl ketones is, however, complex [17]). The substituted carbon atom migrates preferentially during the reaction of 2-alkyl-substituted *cyclo*pentanones and *cyclo*hexanones, also of 2-cyano*cyclo*hexanone.[18] Fusco and Rossi [19] have found the phenyl group to migrate to the preponderating extent in the Schmidt reactions of a series of ketones $C_6H_5\cdot CO\cdot CH_2X$, where X represents the electron-attracting substituents CN, $CO\cdot NH_2$, CO·NHPh, NO_2, SO_2Ph.

In methyl α-methylstyryl ketone the larger group migrates preferentially, and in methyl styryl ketone the smaller.[3] The reactions of a number of ketones Ar·CO·Ph, in which Ar is an *ortho*-substituted aryl group or an analogous polycyclic group, have been examined. With the following the larger group migrates preferentially: 2-nitro-, 2-phenyl-, 2 : 4 : 6-trimethyl-benzophenone; [20] 3-benzoyl-2 : 5-dimethylthiophen.[21] In the following the smaller group migrates preferentially: 2-methyl-, 2-chloro-, 2-bromo-benzophenone; [20] 1-benzoylnaphthalene; [21] 1-benzoylphenanthrene.[22] The reaction of *o*-aroylbenzoic acids has been shown to proceed *via* a cyclic cation the formation of which involves the intervention of the carboxyl group,[23] whence these compounds cannot be regarded as simple 2-substituted benzophenones.

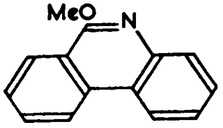
The results cited above do not lead to simple rules for the prediction of migratory aptitudes in the ketonic Schmidt reaction; bulk in the vicinity of the carbonyl group may be a factor, but two of the instances for which this is most apparent, the reactions of the above alkyl phenyl ketones and ω-substituted acetophenones, are such that the migratory aptitudes of the alkyl groups could be regarded as being promoted by inductive electron-release and inhibited by inductive electron-withdrawal.

Smith does not state explicitly at what point the cation (VI) takes up a molecule of water. The acid reagent commonly used in the Schmidt reaction is concentrated sulphuric acid, which may effect the dehydration of (IV) to (V), but is unlikely to liberate water to convert (VI) into (VII), whence it is concluded that this last step would occur when the sulphuric acid solution is diluted with water at the end of the reaction. This

---

[17] Zook and Paviak, *J. Amer. Chem. Soc.*, 1955, **77**, 2501.
[18] Shechter and Kirk, *ibid.*, 1951, **73**, 3087.
[19] Fusco and Rossi, *Gazzetta*, 1951, **81**, 511.
[20] Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 431.
[21] Badger, Howard, and Simons, *J.*, 1952, 2849.
[22] Dice and Smith, *J. Org. Chem.*, 1949, **14**, 179.
[23] Arcus and Coombs, *J.*, 1953, 3698.

circumstance offers a means of testing the validity of the mechanism, for replacement of water by methanol as nucleophilic diluent would be expected to lead to the formation of the methoxy-compound (VIII). If a fluorenone is used, then a 9-methoxyphenanthridine (IX) is the expected product on Smith's mechanism.



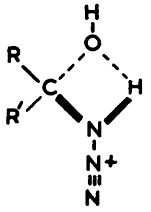
(IX)

The test was first made with 2-nitrofluorenone; part of the sulphuric acid solution from the Schmidt reaction was poured into dry methanol and part into ice and water: each gave a mixture of 2- and 7-nitrophenanthridone. The test was then carried out with fluorenone, which yields a single product, phenanthridone. It was originally intended to employ sulphuric acid containing sufficient free sulphur trioxide to combine with the water supposed to be eliminated as in (IV) $\longrightarrow$ (V), but this reagent was found to sulphonate fluorenone completely. Reaction was therefore effected in 100% sulphuric acid; fluorenone dissolved in this acid, but, on dilution of the solution with water, 99·5% was recovered. The sulphuric acid solution from the Schmidt reaction was added to cold, dry methanol; phenanthridone was precipitated, and a pure specimen was obtained by recrystallisation from the non-hydroxylic solvent toluene.

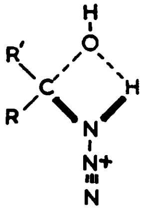
There appears to be no probable mechanism whereby 9-methoxyphenanthridine, if it were formed during the above procedure, could become converted into phenanthridone. However, this compound has been prepared by the reaction of 9-chlorophenanthridine with methanolic sodium methoxide; a solution of 9-methoxyphenanthridine in methanolic sulphuric acid containing 1 mol. of water relative to the methoxy-compound gave no precipitate, and 94% of the 9-methoxyphenanthridine was recovered.

It is concluded that neither re-hydration of (VI), nor the formation of (V) by dehydration, takes place during the Schmidt reaction.

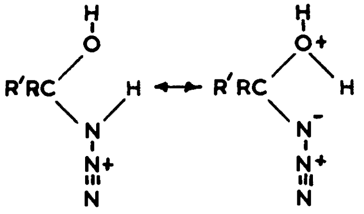
The following structure is proposed for the intermediate in the ketonic Schmidt reaction. Inspection of a model of the protonated azide (IV) shows that the hydrogen atom bonded to nitrogen closely approaches the hydroxylic oxygen atom when the molecule is in the conformations (X) and (XI), and it is suggested that a hydrogen bond is formed between the nitrogen and the oxygen atom, giving rise to a four-membered ring. The ring nitrogen is considered to possess a pyramidal configuration, whence two geometrically isomeric forms, spatially represented in (X) and (XI), are possible for the protonated azide. The structures which contribute to the hydrogen bond are shown in (XII) and (XIII).



(X)



(XI)



(XII) (XIII)

The group which is *trans* to the N_2-group migrates when the latter separates; form (X) thus yields R'·CO·NHR, and form (XI) yields R·CO·NHR'. [Both (X) and (XI) possess an optical isomer, and each is representative of a racemic mixture; however, this is not relevant to the mechanism.]

The configuration of the $>N-N_2^+$ unit relative to the groups R and R' would be expected to depend partly on the polar forces between these structures, and partly on the bulk of these groups in the neighbourhood of the unit.

2 : 7-*Dinitrophenanthridine*.—This compound has been synthesised by the following method: the Schmidt reaction with 2 : 7-dinitrofluorenone[5] gave 2 : 7-dinitrophenanthridone; this was converted into 9-chloro-2 : 7-dinitrophenanthridine and thence, *via* the toluene-*p*-sulphonhydrazide, into 2 : 7-dinitrophenanthridine.

EXPERIMENTAL

M. p.s are corrected.

The preparation of 2-methoxy-, 2-nitro-, and 3-nitro-fluorenone has been described.[24]

The Schmidt Reaction.—2-Methoxyfluorenone. Sulphuric acid (98%; 22 ml.) was added dropwise to a cooled and stirred suspension of sodium azide (7·3 g.) in chloroform (75 ml.). After 10 min., the temperature was raised to 25° and 2-methoxyfluorenone (15·6 g.) was added in small portions during 2 hr. After a further hour, water was added and the whole was shaken; there separated a brown solid (12·4 g.), m. p. 195—215°, which was collected, dried, and sublimed at 200°/0·001 mm. Eight fractions of a cream-coloured microcrystalline solid (5·95 g.) were obtained, all of which melted within the range 229—241°; the non-volatile black residue (4·0 g.) contained nitrogen and sulphur. The last fraction (0·50 g.), m. p. 237—241°, on recrystallisation from pyridine gave needles of 2- and 7-methoxyphenanthridone (0·35 g.), m. p. 239—242° (Found: C, 74·4; H, 4·95; N, 6·4. Calc. for $C_{14}H_{11}O_2N$: C, 74·65; H, 4·9; N, 6·2%). The rest of the sublimate was heated under reflux for 4½ hr. with phosphorus oxychloride (25 ml.), and the solution was cooled and poured on ice; the precipitate (5·55 g.), m. p. 104—112°, was collected, dried, and fractionally crystallised from light petroleum (b. p. 60—80°, 500 ml.). The first crop (2·4 g.), m. p. 133—135°, yielded on recrystallisation 9-chloro-2-methoxyphenanthridine (1·7 g.), m. p. 136—137°. Further crops (2·6 g., m. p.s in the range 94—104°) gave on recrystallisation 9-chloro-7-methoxyphenanthridine (1·95 g.), m. p. 101—103°, raised to 104° by a second recrystallisation. Walls [5] records m. p. 137·5° for 9-chloro-2- and m. p. 107° for 9-chloro-7-methoxyphenanthridine.

2-Nitrofluorenone. To a stirred solution of 2-nitrofluorenone (5·0 g.) in sulphuric acid (28 ml.) at 0°, sodium azide (2·8 g.) was added during 1 hr. After a further 30 min. the solution was poured on ice, and the yellow solid which separated (5·3 g.), m. p. 326—336°, was collected, washed, and dried. This material (500 mg.) was sublimed at 210°/0·5 mm. in 11 fractions: the first four (total 30 mg.) melted at 282—308° and on crystallisation from pyridine formed a microcrystalline powder (20 mg.) having m. p. 298—303°; the last 7 fractions (total, 390 mg.), m. p. 335—342°, on recrystallisation from pyridine yielded 2-nitrophenanthridone (230 mg.), m. p. 360°. Nunn, Schofield, and Theobald [7] record m. p. 357—358° for 2-nitrophenanthridone and m. p. 286—287° for the 1 : 2 complex of 2- and 7-nitrophenanthridone.

Recrystallisation from pyridine (700 ml.) of the crude material (25 g.; m. p. 325—335°) from a second experiment, with 25 g. of 2-nitrofluorenone, yielded 2-nitrophenanthridone (15 g.), m. p. 358—359°. The conversion of this specimen into 9-chloro-2-nitrophenanthridine, and thence into 2-nitrophenanthridine is described in Part III.[4]

Methanol (700 ml.) was heated for 4 hr. under reflux with, then distilled from, freshly ignited quicklime (140 g.); 50 ml. of the distillate were warmed with magnesium (3 g.) and a crystal of iodine; a vigorous reaction occurred, and the solution of magnesium methoxide was then added to the rest of the distillate which was then heated under reflux. Next, the methanol was distilled into a thoroughly dried three-necked flask fitted with a dropping funnel and a mercury-sealed stirrer. Meanwhile, the reaction between 2-nitrofluorenone (5·0 g.), sodium azide, and sulphuric acid was carried out as above. The greater part of the sulphuric acid solution was then added dropwise to the stirred methanol, which was cooled in ice and salt. The precipitate was collected, washed with absolute ethanol, then with light petroleum, and dried in an oven; it (4·4 g.) had m. p. 325—329°. The rest of the sulphuric acid solution was poured on ice and yielded a product having m. p. 321—325°, and m. p. 322—326° when mixed with the product from methanol-dilution. The slightly higher m. p. of the latter product is attributed to the extraction of impurities by the methanol.

3-Nitrofluorenone. (M. p.s in this section are uncorrected.) This compound (5·0 g.) was subjected to the Schmidt reaction by the procedure described for the 2-isomer. Of the product (5·2 g.), m. p. about 340°, 4·7 g. were sublimed at 220°/0·1 mm. in 22 fractions, all yellow powders; the residue was a black amorphous solid. Fraction 4 (15 mg.), m. p. 333—340°, was analysed (Found: C, 64·7; H, 3·55. Calc. for $C_{13}H_8O_3N_2$: C, 65·0; H, 3·35%). The highest-melting fraction (56 mg.), m. p. 365—367°, on crystallisation from pyridine yielded 3-nitrophenanthridone (38 mg.), cream-coloured needles, m. p. 372—374° alone and when mixed with the authentic compound, having m. p. 372°, prepared by the nitration of phenanthridone according to Moore and Huntress.[25] The first, and lowest-melting, fraction (83 mg.), m. p. 332—334°, on crystallisation from pyridine yielded yellow needles (41 mg.), m. p. 333—335°, of (below) the

---

[24] Arcus and Coombs, *J.*, 1954, 3977.

[25] Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 1332.

1 : 1 eutectic mixture of 3- and 6-nitrophenanthridone. By the use of authentic specimens of 3- and 6-nitrophenanthridone (the latter, m. p. 368°, was prepared as described in Part III [4]), a m. p.–composition curve was constructed by the method previously given; [4] the electrically heated m. p. apparatus was preheated to 320°. The facts that the m. p. of the first fraction is very nearly that of the eutectic, and that 68% of 3-nitrophenanthridone was isolated from the highest-melting fraction, demonstrate all the fractions to contain 50% or more of the 3-isomer. This was verified by determination of m. p.s of mixtures of an intermediate fraction with 3- and with 6-nitrophenanthridone. The compositions of the fractions were read off from the curve, whence the sublimate was found to contain 2·43 g. of 3- and 1·10 g. of 6-nitrophenanthridone.

6-Nitrophenanthridone (%)	20	40	50	60	80
M. p. (first determ.)	360°	342°	337°	344°	355°
(second determ).	358°	339°	335°	345°	357°

2 : 7-*Dinitrofluorenone*. 2 : 7-Dinitrofluorene [26] (45 g.), glacial acetic acid (1·5 l.), and chromium trioxide (36 g.) were heated under reflux for 75 min., and allowed to cool. The solid which separated was collected, washed with water, and crystallised from pyridine (700 ml.); it yielded yellow needles of 2 : 7-dinitrofluorenone (30 g.), m. p. 295—296° (Schultz [27] records m. p. 291—292°, but gives no details of the preparation). Reaction of this compound (15·0 g.) with sulphuric acid and sodium azide according to Walls [5] gave 2 : 7-dinitrophenanthridone (15·6 g.), m. p. >380°, which was converted into 9-chloro-2 : 7-dinitrophenanthridine (10·5 g.), m. p. 225—227°, by the method of Albert,[28] who records m. p. 225°.

A solution of this compound (10·5 g.) and toluene-*p*-sulphonhydrazide (10·0 g.) in chloroform (850 ml.) was boiled under reflux for 60 hr. in the course of 5 days, and the crystalline precipitate (14·8 g.), m. p. 200° (decomp.), was collected. In 0·5N-sodium hydroxide (1·5 l.) it gave an almost black suspension which when stirred at 80° evolved nitrogen. After 80 min. the suspension was cooled, and the solid was collected and extracted with boiling 5N-hydrochloric acid (200 ml.). The extracts were poured into an excess of 5N-sodium hydroxide; there separated an orange solid (3·0 g.), m. p. 290—300°, which was sublimed *in vacuo*; the sublimate, on crystallisation from chlorobenzene, yielded 2 : 7-*dinitrophenanthridine*, yellow needles, m. p. 302^{c} (Found : C, 58·2; H, 2·6; N, 15·3. $C_{13}H_7O_4N_3$ requires C, 58·0; H, 2·6; N, 15·6%).

Fluorenone : *methanol dilution*. Fluorenone (2·0 g.) was dissolved in oleum (containing 83·4% of SO_3, *i.e.*, 9·5% of free SO_3; 15 ml.), and the solution was poured on ice; a clear aqueous solution resulted. Sulphuric acid (100%) was prepared by the following method, based on Brand's observations; [29] to acid somewhat below this strength, oleum (20% of free SO_3) was added from a burette until a permanent fuming was obtained; sulphuric acid (95%) was similarly added until fuming just ceased. The acid so prepared had $d_{15\cdot5}^{15\cdot5}$ 1·8393; Fairlie [30] records $d_{15\cdot5}^{15\cdot5}$ 1·8391 for 100·0% sulphuric acid.

Fluorenone (2·042 g.) was stirred with ice-cold sulphuric acid (100%; 15 ml.) for 1 hr. The resulting solution was poured on ice; the solid which separated was collected in a sintered glass crucible, washed with water, and dried, in air at 38°, then *in vacuo*, to constant weight (2·029 g.).

To a stirred solution of fluorenone [distilled, and recrystallised from benzene–light petroleum (b. p. 40—60°); m. p. 83°; 4·5 g.] in sulphuric acid (100%; 60 g.), in a flask protected by a calcium chloride tube and cooled in ice, sodium azide (3·25 g.) was added from a closed hopper during 1½ hr. Stirring was continued for a further hour. The solution was then added dropwise to chilled dry methanol (650 ml.) prepared and used as described for 2-nitrofluorenone. A brown solid separated; it was collected, washed with dry methanol and with light petroleum (b. p. 40—60°), and dried *in vacuo*; the greater part was soluble in hot toluene (dried over sodium; 340 ml. of boiling toluene dissolve 1·0 g. of phenanthridone) from which it was recrystallised. The experiment was repeated. There were obtained :

	Original product		1st recrystalln.		4th recrystalln.	
	wt.	m. p.	m. p.	mixed m. p.*	m. p.	mixed m. p. *
(i)	3·2 g.	282·5—290·5°	291—293·5°	293·5—294°	293·5—294°	294—294·5°
(ii)	2·8 g.	281·5—287·5°	291—292·5°	292·5—294·5°	293·5—294·5°	293·5—294·5°

* With a standard specimen of phenanthridone having m. p. 293·5—294·5°.

---

[26] Courtot, *Ann. Chim.* (*France*), 1930, **14**, 83.

[27] Schultz, *Annalen*, 1880, **203**, 104.

[28] Albert, *J.*, 1948, 1284.

[29] Brand, *J.*, 1946, 585.

[30] Fairlie, " Sulphuric Acid Manufacture," Reinhold Publ. Corp., New York, 1936, p. 611.

Phenanthridone (2·0 g.) and phosphorus oxychloride (10 ml.) were boiled under reflux for 9 hr. The solution was poured into stirred ice–water; stirring was continued for 1 hr. and the solid product was collected, dried *in vacuo*, and extracted with ether (60 ml.). The extract yielded 9-chlorophenanthridine (1·8 g.), m. p. 115—116°, and m. p. 118·5° after repeated recrystallisation from ether (Graebe and Wander[31] record m. p. 116·5°). Preparations on a larger scale gave smaller percentage yields.

Sodium (1·54 g.) was allowed to react with dry methanol (61 ml.), and to the cooled solution was added 9-chlorophenanthridine (13·0 g.); the whole was boiled under reflux for 1 hr. and poured into ice–water. The solid which separated was collected, washed, and dried *in vacuo*; the greater part of the product dissolved in hot light petroleum (b. p. 60—80°), whence separated 9-*methoxyphenanthridine* (11·0 g., m. p. 42—48°) which, after further recrystallisation, formed needles, m. p. 54·5° (Found: C, 80·25; H, 5·35; N, 6·6. $C_{14}H_{11}ON$ requires C, 80·35; H, 5·3; N, 6·7%).

A solution of 9-methoxyphenanthridine (5·190 g.) in dry methanol (95 ml.) was added to a solution, cooled to −8°, prepared from dry methanol (600 ml.), sulphuric acid (100%, 30 ml.), and a 5N-solution of water in methanol (5·0 ml.). After 15 min., during which it remained clear, the solution was poured into a stirred mixture of sodium carbonate (127 g.) and ice (1½ kg.). After 1 hr., water was added and the whole was extracted with light petroleum (b. p. 40—60°; 3 × 150 ml.). The extract was washed with aqueous sodium carbonate, and with water, and dried (Na_2SO_4), and the solvent distilled. The 9-methoxyphenanthridine so recovered was dried *in vacuo* over sulphuric acid and paraffin wax to constant weight (4·881 g.); it had m. p. 51° and, after three recrystallisations from light petroleum (b. p. 60—80°), m. p. 54°, mixed m. p. 54·5°.

Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Limited for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, October 4th*, 1955.]

[31] Graebe and Wander, *Annalen*, 1893, **276**, 250.