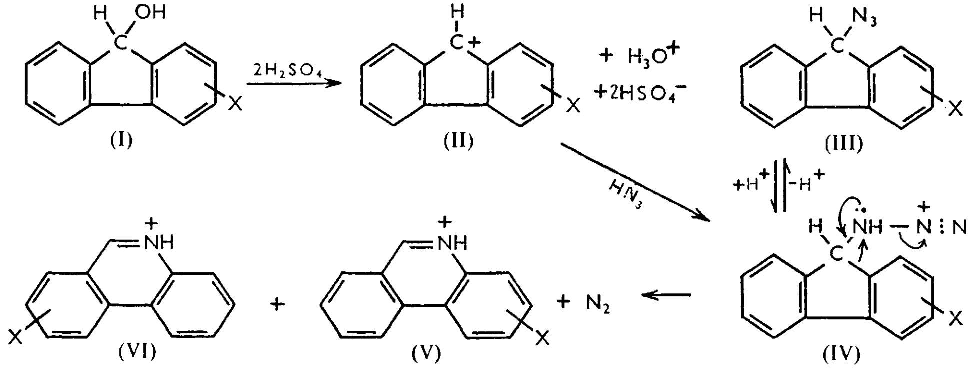
153. *Reactions of Organic Azides. Part VIII.*[1] *Kinetics of the Rearrangement of* 9-*Azidofluorene in Sulphuric–Acetic Acid.*

By C. L. Arcus and J. V. Evans.

Rearrangement, in sulphuric–acetic acid, of 9-azidofluorene to phenanthridine is substantially of the first order in the azide with $\log_{10}$ rate linear with $-H_0$ for the medium, at slope slightly greater than unity and an activation energy of $\sim$23·4 kcal./mole. It is concluded that reaction proceeds *via* the monoprotonated azide (which probably exists largely as the ion-pair with bisulphate ion), and that nitrogen-release and the act of rearrangement are simultaneous.

The conversion, by reaction with hydrazoic and sulphuric acid, of fluoren-9-ols into phenanthridines has been described and discussed in Parts I,[2] III,[3] IV,[4] and VII,[1] attention having been directed to separation and characterisation of mixtures of isomeric phenanthridines, the mechanism of the reaction, and the influence of substituents.

The following observations show that reaction proceeds through formation of the azide (as its proton-adduct): (*a*) from the products of the reaction with fluoren-9-ol [2] and 9-*tert.*-butylfluoren-9-ol,[4] the 9-azidofluorene was isolated; (*b*) on reaction with sulphuric acid, 9-azido-,[2] 9-azido-9-phenyl-,[1] and 9-azido-2-methoxy-fluorene [3] yielded respectively phenanthridine and 9-phenyl- and 2- and 7-methoxy-phenanthridine, the products which are obtained from reaction of the corresponding fluoren-9-ols with hydrazoic and sulphuric acid. In the reaction of a fluorenol with these acids, the function of the sulphuric acid is two-fold: (i) to convert the alcohol (I) into a carbon cation (II) which, on combination with hydrazoic acid, yields the proton-adduct (IV) of the azide (III); (ii) to maintain a



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[1] Part VII, Arcus, Marks, and (in part) Coombs, *J.*, 1957, 4064.
[2] Arcus and Mesley, *J.*, 1953, 178.
[3] Arcus and Coombs, *J.*, 1954, 4319.
[4] Arcus and Lucken, *J.*, 1955, 1634.

substantial proportion of the azide in the protonated state, it being the proton-adduct, not the free azide, which undergoes rearrangement to the phenanthridinium ion (V, VI). That this is so, is shown by observations on secondary azidofluorenes. Thus, although 9-azidofluorene in sulphuric acid liberates nitrogen with rearrangement to the phenanthridinium ion, on long storage or on being heated alone it loses nitrogen to yield 9-iminofluorene.[2] Analogous observations relate to 9-azido-2-nitrofluorene:[3] this compound was never isolated, but 2-nitrofluoren-9-ol gave 2- and 7-nitrophenanthridine on reaction with hydrazoic and sulphuric acid, whereas heating 9-chloro-2-nitrofluorene with sodium azide yielded 9-imino-2-nitrofluorene, presumably by uncatalysed decomposition of the azide. Finally, 9-azido-1 : 2-benzofluorene, heated with trifluoroacetic acid, yields 1 : 2- and 7 : 8-benzophenanthridine, whilst, heated alone, it forms 1 : 2-benzofluorenone imine.[1]

The complexity of the conversion of fluorenol into phenanthridine, and the dual rôle of the strong acid, might be expected to render interpretation of kinetic results for the overall reaction somewhat difficult. It has however been concluded[4] (at least for the two instances in which the azidofluorene accumulated in the reaction mixture to such an extent that it was isolated) that the last stage, (IV) ⟶ (V, VI), is rate-controlling. It was therefore decided to further the investigation of the rearrangement by determining the rate of conversion of 9-azidofluorene into phenanthridine in anhydrous sulphuric–acetic acid solutions. Values of the Hammett acidity function, H_0, for sulphuric–acetic acid mixtures, of concentrations suitable for the rearrangement, have been determined by Hall and Spengeman.[5]

EXPERIMENTAL

M. p.s are corrected.

9-Azidofluorene.—To a hot solution of aluminium *iso*propoxide (from aluminium foil, 50 g.; mercuric chloride, 1 g.; propan-2-ol, 800 ml.) was added fluorenone (61 g.) in benzene (250 ml.); the whole was boiled under reflux for 4 hr., the lowest-boiling (acetone) fraction being allowed to distil. Excess of solvent was then distilled under reduced pressure and the viscous residue was poured with stirring into ice-cold 3N-sulphuric acid (3 l.). The precipitate was collected, washed with this acid, then with water, and dried. It (50·5 g.; m. p. 142—143°) was heated with benzene (500 ml.) containing charcoal (1 g.); from the filtered solution there separated fluoren-9-ol (43·5 g.) having m. p. 153—155° and, after further recrystallisation, m. p. 156°. This material was converted by Arcus and Mesley's methods[2] into 9-chlorofluorene (m. p. 90—91°), then into 9-azidofluorene. The latter was recrystallised as follows: it (4·7 g.; m. p. 40—42°) was dissolved in warm 96% ethanol (45 ml.), and the solution was treated with charcoal (0·5 g.) and filtered; on addition of water (4 ml.) to the filtrate, 9-azidofluorene separated as colourless needles (2·7 g.), m. p. 44·5° unchanged by further recrystallisation. The azide used in the kinetic runs was colourless material of m. p. $\nless$44°; it was stored in a stoppered bottle kept in a desiccator in the dark; under these conditions it was stable for four weeks, but was used within two weeks.

Fluoren-9-ol (3·6 g.) was stirred with sodium azide (2·6 g.), chloroform (40 ml.), and trichloroacetic acid (40 g.) for 2½ hr. at 30°, and the whole was poured into ice-water; the fluorenol (3·5 g.), m. p. 156—157°, was recovered.

Sulphur trioxide was distilled from oleum (26% of free SO_3) into sulphuric acid (" AnalaR "; 98%). The fuming acid so obtained was adjusted to 100% by dilution with the 98% acid and titration to cessation of fuming as described earlier.[6] This acid was cooled at 0° until half had solidified; the liquid was rejected. The freezing point of the acid so prepared was determined in a simplified form of Gillespie, Hughes, and Ingold's apparatus;[7] additions of fuming or 98% acid were made where required, in order to attain the maximum freezing point of 10·36—10·39° (uncorr.); little adjustment was necessary.

Acetic acid was twice crystallised by partial solidification, distilled, then thrice recrystallised,

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[5] Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2489.

[6] Arcus, Coombs, and Evans, *J.*, 1956, 1498.

[7] Gillespie, Hughes, and Ingold, *J.*, 1950, 2475.

attaining constant f. p. (determined as above) 16·45°. Sulphuric and acetic acid were kept in capped stoppered bottles.

One ml. of acetic acid dissolved 0·3 g. of 9-azidofluorene, and 0·4 g. of phenanthridine, at 25°.

Rate Measurements.—The all-glass reaction vessel comprised a lower, conical, flat-bottomed bulb (*A*) and an upper spherical bulb (*B*); the contents of *B* could be run into *A* through a tap of 4 mm. bore; a pressure-equalising tube connected the tops of *A* and *B*; *A* was fitted with a stoppered (B14) side-arm, and a similar joint connected the top of *B* to the nitrometer. Bulb *B* was placed to one side of the axis of *A*, whereby a shorter form of apparatus was attained.

9-Azidofluorene was weighed into *A*. By pipettes, and the use of a "Pumpett," the requisite amount of sulphuric acid was placed in *B*, and the vessel was reweighed; 50 ml. of acetic acid were then placed in *B* and 10 ml. in *A*, and the whole was again weighed. A Polythene-covered soft-iron stirrer, 3 cm. long, was placed in *A*. The acids in *B* were mixed by rotation of the bulb.

The reaction vessel was then attached to the nitrometer, the tap and joints having been lubricated with a Silicone grease, and immersed in the thermostat. The bulb *A* was placed over a motor-driven rotating magnet; the latter was contained in a water-tight brass box completely immersed in the thermostat bath and fitted with vertical brass tubes acting as vents and carrying the electrical leads. The nitrometer, from which air had been displaced by dry nitrogen, contained transformer oil, and was surrounded by a jacket through which water from the thermostat was circulated by a pump at 300 ml./min. The whole was kept for 1 hr. with the stirrer operating, whereby constant temperature and initial nitrometer reading were attained. The tap connecting *B* with *A* was then opened fully, and the stopwatch started. The time of discharge through the tap was 7—15 sec. depending on the viscosity of the sulphuric–acetic acid solution. Nitrometer readings, at atmospheric pressure, were taken at one-minute intervals for the first 5 min., thereafter less frequently, and finally at 24 hr. In many runs observations were made for a further period. The volume of nitrogen obtained when no further evolution was observed averaged 97·6% of the theoretical. Exceptions were runs at the two lowest acidities at 25°, the latter parts of which were sluggish.

As the run proceeded, the solution became orange and towards the end turbid. It was filtered through a No. 1 sintered-glass filter, and the vessel and precipitate were washed with acetic acid. The precipitate, after being washed with water and methanol, formed a buff powder, m. p. >300°. In ten experiments it averaged 5·2% of the weight of azide used.

The acidic filtrate and washings were diluted with water to 200 ml., neutralised, with cooling and stirring, by ammonia (*d* 0·88, 1 part; water 2 parts), further ammonia (50 ml.) then being added. The precipitated phenanthridine was collected on a No. 1 sintered-glass filter, washed with dilute aqueous ammonia, and dried. It had m. p. 101—103°, and, after recrystallisation from light petroleum (b. p. 60—80°), m. p. 109°. In seven experiments the yield of phenanthridine averaged 94·2%.

By the procedure of mixing the sulphuric acid with the bulk of the acetic acid, and allowing the solution to attain thermostat-temperature before adding it to a solution of the azide in a small portion of the acetic acid, most of the heat of dilution was dissipated before the reaction began. Both in the presence of azide (0·6 g.) and in its absence, where the final concentration of sulphuric acid was 36·5%, the maximum rise in temperature above that of the thermostat, when the contents of *B* and *A* were mixed, was 0·85°; it fell to 0·1° in 30 min.; with acid finally containing 28·5% sulphuric acid, the maximum rise was 0·5°.

In experiments preliminary to the main series it was found that phenanthridine, added initially with the azide, decreased the reaction rate, but did not appreciably lower the final volume of nitrogen evolved. At the ends of the present runs, the excess of sulphuric acid over phenanthridine was from 20- to 106-fold.

It was noticed in experiments without azide that, during the first 2 min. after the contents of *B* had run into *A*, there was a small evolution of gas. This is ascribed to displacement of gas dissolved in the acetic acid in *A* on addition of the sulphuric–acetic acid. For acids finally containing 25·5 and 36·5% sulphuric acid, at 25°, the volume evolved in each case averaged 1·2 ml.; by extrapolation of the readings for the first few minutes of azide runs back to zero time, it was found that an identical initial evolution had occurred, *i.e.*, that the latter is a physical displacement unaffected by the presence of azide. The initial evolution was markedly less when higher reaction-temperatures were used. For the slower azide runs, correction for the initial evolution was made by extrapolation as above, and for the fastest runs by addition to the pre-mixing nitrometer-reading of the volume found to be evolved in a parallel non-azide run.

Vapour pressures of sulphuric–acetic acid mixtures have not been recorded; corrections (about 0·01 atm. at 25°) were made on the assumption that acetic acid is dimeric, and that sulphuric acid forms a 1 : 1-molecular complex with acetic acid. In a solution composed of p moles of sulphuric and q of acetic acid, the molar fraction of dimer is $(q - p)/(q + p)$, and the recorded vapour pressures of acetic acid were reduced by this factor. The volume of evolved nitrogen, reduced to ml. at N.T.P., x, was plotted against time, t (min.); $t_{0\cdot5}$ and $t_{0\cdot7}$, the times for evolution of half and seven-tenths of the volume (a) equimolar with the weight of azide taken, were ascertained. $\Delta x/\Delta t$ was plotted against t, and $\log_{10} (\mathrm{d}x/\mathrm{d}t)$ then plotted against $\log_{10} (a - x)$. Such plots were substantially linear, and the initial intercept gave $\log_{10} (\mathrm{d}x/\mathrm{d}t)_{t=0}$, from which was derived the initial pseudo-first-order constant k_i, in min.$^{-1}$. The slope of the logarithmic plot was in general greater than unity, the average dependence on $(a - x)$ being to power 1·20. Of the minor factors modifying the individual run, detailed above, initial temperature rise and the formation of phenanthridine tend to raise the apparent order; the influence on order of the formation of a small amount of non-phenanthridine by-product is not readily deducible. The determination of k_i, $t_{0\cdot5}$, $t_{0\cdot7}$, yielding comparable values at three points in the course of each run, is considered to be the most satisfactory treatment of the experimental data.

RESULTS AND DISCUSSION

Fluorenone was satisfactorily reduced to fluoren-9-ol by aluminium *iso*propoxide; reduction with this reagent is preferable to that, used hitherto, with sodium amalgam. Unlike 9-phenyl- and 1 : 2-benzo-fluoren-9-ol, the unsubstituted compound did not yield the azidofluorene on treatment with trichloroacetic acid and sodium azide; it was recovered.

A series of runs with different initial concentrations of 9-azidofluorene was carried out at 25°, in acetic acid containing 34·1% sulphuric acid, whence H_0 is $-4{\cdot}01$. The plot of $\log_{10} (\mathrm{d}x/\mathrm{d}t)_{t=0}$ *versus* $\log_{10} a$ (Fig. 1) is substantially linear at slope 1·09. $\mathrm{Log}_{10}\, t_{0\cdot5}$ and $\log_{10} t_{0\cdot7}$, when similarly plotted, have slope $-0{\cdot}04$ and $-0{\cdot}02$; it can be shown [8] that

$$\log t_{\text{fraction}} = \text{Constant} - (n - 1) \log a$$

where t_{fraction} is the time required for a given fraction of the total reaction to occur, and n the reaction-order, whence, in the present instance, the times for half and seven-tenths completion yield reaction-order 1·04 and 1·02 respectively. From the three sets of data it is concluded that the reaction is essentially first-order in 9-azidofluorene; this accords with the mechanism, involving the rate-controlling decomposition of the protonated azide, which has been deduced for the rearrangement on non-kinetic grounds.

Runs were next made with sulphuric–acetic acid solutions containing from 10·1 to 36·5% sulphuric acid, and hence having H_0 from $-2{\cdot}87$ to $-4{\cdot}85$. The results are given in Fig. 2, where $\log_{10} k_\mathrm{i}$, $-\log_{10} t_{0\cdot5}$, and $-\log_{10} t_{0\cdot7}$ are plotted against $-H_0$. (The values of $-\log_{10} t_{0\cdot5}$ are equal to the logarithms of the pseudo-first-order reaction constants measured over the times for half reaction, together with a numerical constant, and similarly for $-\log_{10} t_{0\cdot7}$.) The slopes of the straight lines drawn through these sets of points are, respectively, 1·03, 1·07, and 1·09.

It is not believed that linearity between log rate and $-H_0$ extends to acidities much below those of Fig. 2. Preliminary experiments, during which practicable conditions for kinetic measurements were being sought, implied that there exists a threshold of acidity below which decomposition does not occur. These experiments also showed reaction, at the same concentration of sulphuric acid, to be markedly faster in nitromethane than in acetic acid.

The data of Fig. 2 imply that the rate-determining step of the reaction proceeds either through the monoprotonated azide (IV; X = H) formed in fractionally small amount

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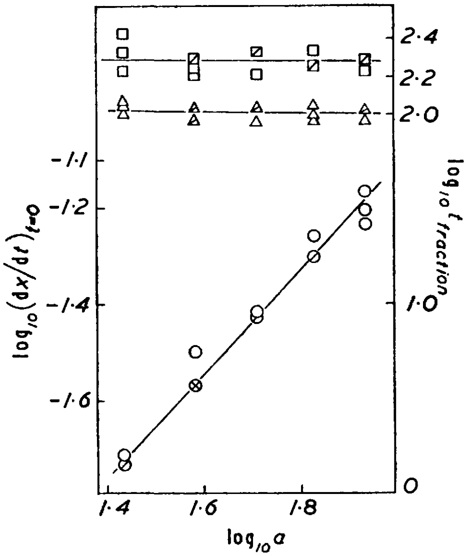
[8] Frost and Pearson, "Kinetics and Mechanism," Wiley, New York, 1953, pp. 40—42.

from the azide (III), or through the diprotonated azide (VIII or IX), formed in fractionally small amount from the otherwise completely monoprotonated azide.

$$R{\cdot}NH{\cdot}\overset{+}{N}{:}N \overset{H^+}{\rightleftharpoons} R{\cdot}\overset{+}{N}H_2{\cdot}\overset{+}{N}{:}N \text{ (VIII) or } R{\cdot}NH{\cdot}\overset{+}{N}{:}\overset{+}{N}H \text{ (IX)}$$

While the second alternative is not excluded, it appears the less probable because rearrangement through (IX) implies the separation of protonated nitrogen, whereas nitrogen has no manifest basic properties, and rearrangement through (VIII) implies either the formation of doubly protonated phenanthridine, or, since accommodation of a second proton is hardly possible, the ejection of a proton at the act of rearrangement.

FIG. 1.



FIGS. 1, 2, and 3.
Rearrangement of 9-azidofluorene in sulphuric–acetic acid.

○ $\log_{10} (dx/dt)_{t=0}$ or $\log_{10} 10^4 k_i$.
△ $\log_{10} t_{0{\cdot}5}$.
□ $\log_{10} t_{0{\cdot}7}$.

Two coincident points are marked /, and three ×.

FIG. 2.

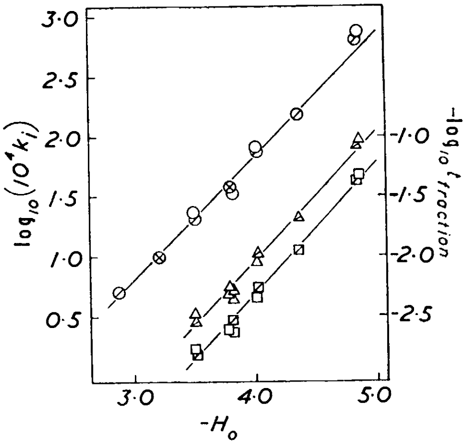
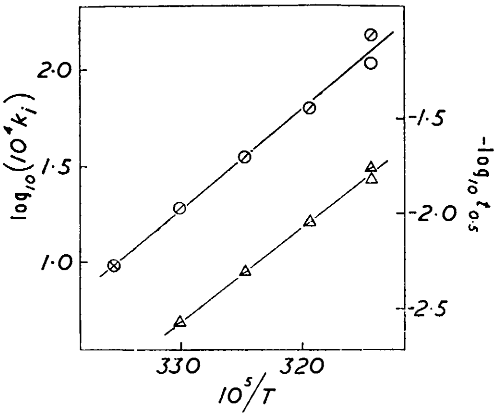


FIG. 3.



Description of some aspects of the mechanism of the acid catalysis requires a brief account of conditions in the sulphuric–acetic acid solution. Acetic acid is considered to exist in the liquid state as the dimer.[10, 11, 12] From the following results it is concluded that sulphuric acid forms a complex with acetic acid: (*a*) the plot of viscosity *versus* composition has a marked maximum at the equimolar point;[13] (*b*) the freezing points of mixtures of the acids may indicate a 1 : 1 compound;[14] (*c*) the heat of dilution of sulphuric by acetic acid is qualitatively large; no measurement appears to have been recorded. The conductometric and potentiometric investigations of Kolthoff and his co-workers,[15] and Smith and Elliott,[16] lead to the conclusion that the sulphuric–acetic acid complex is mainly a hydrogen-bonded entity, in equilibrium with a relatively small proportion of the ion pair $CH_3{\cdot}CO_2H_2^+HSO_4^-$, which in turn is dissociated only to a small extent into the free ions. The last authors find the classical dissociation constant ($[CH_3{\cdot}CO_2H_2^+][HSO_4^-]/[H_2SO_4]$) of sulphuric acid in acetic acid containing 0·12% of water to be $7{\cdot}4 \times 10^{-9}$.

The species present in the solution which are capable of donating a proton to the azide are, therefore, the hydrogen-bonded sulphuric–acetic acid complex, the ion-pair, above, and the free ion $CH_3{\cdot}CO_2H_2^+$, their aggregate protonating effect being measured by the activity of the hydrogen ion as deduced from the indicator studies on which H_0 is based. From the evidence on ionic aggregation in acetic acid, it is probable that the protonated azide and the phenanthridinium ion exist in solution largely as the ion-pairs with bisulphate ion, and that the rearranging entity is an ion-pair rather than a free cation.

Finally, sets of runs were carried out at 5° intervals from 25° to 45°, at constant initial azide concentration, in acetic acid containing 17·2% of sulphuric acid, whence the medium had (at 25°) H_0 $-3{\cdot}21$. Plots of $\log_{10} k_i$ and $-\log_{10} t_{0{\cdot}5}$ against $1/T$ (Fig. 3; $t_{0{\cdot}7}$ was not used because, at the acidity applying in this series, at the lower temperatures, reaction becomes sluggish in the latter part of the run) yield values 24·0 and 22·8 kcal./mole for the activation energy of the rearrangement.

Rates of decomposition of azido-diphenylmethanes and -1 : 1-diphenylethanes in sulphuric–acetic acid have recently been reported by Gudmundsen and McEwen.[17] These authors obtained pseudo-first-order rate constants for approximately the first 50% of completion, and found the logarithms * to be linear, at unit slope, with values of $-H_0$ for the medium; for azidodiphenylmethane, the energy of activation was found to be 21·2 kcal./mole. These experimental findings are similar to those of the present work. However, the above authors deduce a mechanism for the decomposition of the azide in which release of nitrogen and rearrangement are not synchronous, but proceed in two stages, the intermediate (XI), of finite life, intervening between the protonated azide and the products of rearrangement.

$$\underset{\text{(X)}}{\mathrm{CRPh(C_6H_4X){\cdot}NH{\cdot}\overset{+}{N}{:}N}} \longrightarrow \underset{\text{(XI)}}{\mathrm{CRPh(C_6H_4X){\cdot}\overset{+}{N}H}} + \mathrm{N_2} \longrightarrow \underset{\text{(XII)}}{\mathrm{CR(C_6H_4X){:}\overset{+}{N}HPh}} + \underset{\text{(XIII)}}{\mathrm{CRPh{:}\overset{+}{N}H(C_6H_4X)}}$$

$$\text{(XIV)}\ \mathrm{CPh(C_6H_4X){:}NH} \qquad \mathrm{COPh(C_6H_4X)}\ \text{(XV)}$$

We do not concur in this deduction and consider reaction to proceed by the mechanism exemplified in [(IV) ⟶ (V) + (VI)], in which rearrangement is simultaneous with release of nitrogen. The findings that nitrogen-evolution is

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* The text states that the rate constants were plotted, but a later equation and Table 1 make it clear that the logarithm is intended.

[9] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, pp. 265, 267.

[10] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159.

[11] Partington, " An Advanced Treatise on Physical Chemistry," Vol. II, Longmans, Green and Co., London, 1951, pp. 160—161.

[12] Landee and Johns, *J. Amer. Chem. Soc.*, 1941, **63**, 2891.

[13] Drucker and Kassel, *Z. physikal. Chem.*, 1911, **76**, 367; Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 243.

[14] Kendall, *ibid.*, 1921, **43**, 1832; Lehrman, *Trans. Amer. Inst. Chem. Eng.*, 1926, **18**, 187.

[15] Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, **56**, 1007; Kolthoff and Bruckenstein, *ibid.*, 1956, **78**, 1.

[16] Smith and Elliott, *ibid.*, 1953, **75**, 3566.

[17] Gudmundsen and McEwen, *ibid.*, 1957, **79**, 329.

of the first order in azide and that the plot of log rate *versus* $-H_0$ has unit slope do not permit distinction between these two mechanisms, since both postulate a unimolecular decomposition of the monoprotonated azide.

However, with regard to the products from Gudmundsen and McEwen's mechanism, it appears probable that the intermediate (XII; R = H), formed from an azidodiphenylmethane, would release a proton to yield the imine (XIV), and, on hydrolysis, the benzophenone (XV). These products are those corresponding to hydrogen-migration, and such products are stated[17] never to have been isolated in any of the azido-reactions of diarylmethanols. In the acid-catalysed decomposition of azidofluorenes, the 9-iminofluorenes and fluorenones, the analogues of (XIV) and (XV), have not been encountered. In contrast, as stated earlier, the imine is the characteristic product of the non-catalysed (*e.g.*, pyrolytic) decomposition of a secondary 9-azidofluorene. Further, with regard to the acid-catalysed reaction, it has been found[4] that a 9-*tert.*-butyl group, which can neither conjugate not hyperconjugate, slows down the rearrangement of the azide, compared with reaction in the presence of groups which can conjugate (ethyl, *iso*propyl, phenyl); this accords with the formation of an aromatic ring simultaneously with nitrogen release but not with the formation of the fluorenyl analogue of (XI), in which such aromatisation does not occur. It is concluded that (XI) is not formed, and that migration synchronises with release of nitrogen.

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