909. *Acylarylnitrosamines. Part VI.* The Rearrangement, Decomposition, and Deacylation of Acylarylnitrosamines.*

By D. H. HEY, J. STUART-WEBB, and GARETH H. WILLIAMS.

It has been confirmed that the azo-coupling and the evolution of nitrogen from solutions of acylarylnitrosamines in benzene have a common rate-determining stage which is the rearrangement of the acylarylnitrosamine into the diazo-ester, *i.e.*, $R'\cdot C_6H_4\cdot N(NO)\cdot COR \longrightarrow R'\cdot C_6H_4\cdot N{:}N\cdot O\cdot COR$. By means of a study of the effects of changes in R and R′, of changes in solvent, and of added acids, bases, and salts, an intramolecular mechanism for the rearrangement is indicated. These results confirm and amplify those obtained simultaneously and independently by Huisgen and his collaborators.

ACYLARYLNITROSAMINES were first used as arylating agents by Bamberger (*Ber.*, 1897, **30**, 366), who considered that an equilibrium was set up in solution between the nitroso-form and the corresponding diazo-ester (*a*), which then underwent reaction with benzene to give a derivative of diphenyl:

$$(a) \qquad Ar\cdot N(NO)\cdot CO\cdot R \rightleftarrows Ar\cdot N{:}N\cdot O\cdot CO\cdot R$$

$$(b) \qquad Ar\cdot N{:}N\cdot O\cdot CO\cdot R + C_6H_6 \longrightarrow C_6H_5\cdot Ar + N_2 + R\cdot CO_2H$$

In support of this view von Pechmann and Frobenius (*Ber.*, 1894, **27**, 651) and Hantzsch and Wechsler (*Annalen*, 1902, **325**, 226) showed that nitrosoacetanilide was obtained both from the nitrosation of acetanilide and from the acetylation of sodium benzenediazoate. The first kinetic measurements on the decomposition of nitrosoacetanilide and some substituted acylarylnitrosamines in benzene and other solvents were made by Grieve and Hey (*J.*, 1934, 1797; 1935, 689) and by Butterworth and Hey (*J.*, 1938, 116), who measured the rate at which nitrogen was evolved. They found that the reaction obeyed a first-order kinetic law and that the rate of decomposition was substantially independent of the nature both of the solvent and of any nuclear substituent in the acylarylnitrosamine. These results were interpreted as involving a rapid tautomeric (cationotropic) rearrangement (reaction *a*), followed by a slow rate-determining homolytic fission of the diazo-ester into free radicals with the concomitant release of molecular nitrogen. The homolytic nature of the subsequent phenylation process was demonstrated by the nature of the products formed when monosubstituted benzene derivatives were phenylated by this method (Hey, Nechvatal, and Robinson, *J.*, 1951, 2892, and earlier papers), while the existence of free-radical intermediates was confirmed by Waters (*J.*, 1937, 113), who showed that metals were attacked when present in the reacting system.

More recently Huisgen and Horeld (*Annalen*, 1948, **562**, 137) have repeated and confirmed some of Grieve and Hey's measurements, and also investigated for the first time the rates of coupling of acylarylnitrosamines with β-naphthol. The latter measurements, some of which have been repeated and confirmed by the present authors, show that for a number of acylarylnitrosamines the rate of azo-coupling is very nearly equal to the rate of evolution of nitrogen (Table 1). The small discrepancies between the two series of rates are probably due to the fact that the coupling experiments are carried out at a very much lower concentration than that at which the rates of evolution of nitrogen are measured.

These results brought to light a new aspect of the chemistry of acylarylnitrosamines and provided a strong indication that both reactions—azo-coupling and evolution of nitrogen—have a common rate-determining stage and that this must be the rearrangement of the acylarylnitrosamine to the diazo-ester, which is the latest intermediate which can be common to both reactions. This observation, however, does not establish conclusively the mechanism of the reactions, and the present work was carried out in order to determine whether or not this scheme provides a satisfactory explanation of all aspects of the chemistry of acylarynitrosamines and, if possible, to establish a mechanism for the

---

* Part V (under former title, Nitrosoacylarylamines), *J.*, 1951, 1521.

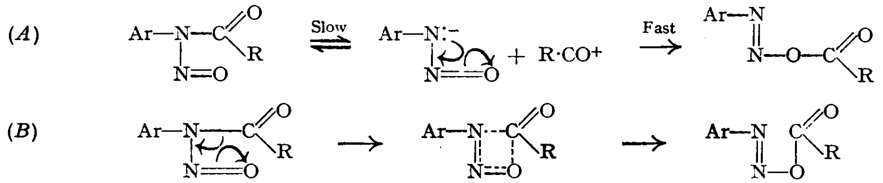
rearrangement itself. During the course of this work investigations on similar lines were being carried out independently by Huisgen and his co-workers (*Annalen*, 1951, **573**, 163, 181; 1951, **574**, 157, 171, 184; 1952, **575**, 174, 197), and also by de Tar (*J. Amer. Chem. Soc.*, 1951, **73**, 1446). The present results, some of which were disclosed in a preliminary note (*Research*, 1951, **4**, 385; see also Hey and Waters, *J.*, 1948, 882), confirm and amplify those obtained by these workers, but in view of the fact that the investigations were carried out simultaneously a detailed comparison of the results obtained in the different laboratories is not here included.

TABLE 1. *Rates of azo-coupling and evolution of nitrogen in benzene solution.*

		First-order rate constants (sec.$^{-1}$) × 10^4			
		Azo-coupling		Evolution of nitrogen	
Acylnitrosoanilide	Temp.	H. and H.	H., S-W., and W.	H. and H.	H., S-W., and W.
Nitrosoformanilide	50°	2·57	2·27	2·62	2·71
Nitrosoacetanilide	25	1·93	2·03	1·48	1·49
Nitrosopropionanilide	15	—	1·93	—	1·17
,, ...	20	3·12	—	2·75	2·36

The establishment of the rearrangement of the acylarylnitrosamine to the diazo-ester as the rate-determining stage in the kinetic measurements based on the rate of evolution of nitrogen necessarily implies that these measurements can no longer be regarded as providing evidence for (or against) a homolytic mechanism. The evidence for homolytic aromatic substitution resides primarily in the analysis of the influence of a substituent group or atom on the substitution process. This has now been placed on a quantitative basis (Hey, Nechvatal, and Robinson, *loc. cit.*; Augood, Hey, and Williams, *J.*, 1952, 2094).

If the rearrangement of the acylarylnitrosamine into the diazo-ester is assumed to be rate-determining, possible mechanisms can be set up and examined. The unimolecular nature of the rearrangement is demonstrated by the original observation by Grieve and Hey (*loc. cit.*) that the decomposition reaction in benzene or other relatively non-polar solvents obeys a first-order kinetic law. This requirement being borne in mind it is apparent that for the uncatalysed rearrangement only two mechanisms are possible, namely a " unimolecular " mechanism (*A*), involving ionic dissociation and recombination of the ions, and an " intramolecular " mechanism (*B*), which is really an internal S_N2 reaction, the oxygen of the nitroso-group functioning as a nucleophilic reagent. A similar intramolecular process was put forward by Huisgen (*Angew. Chem.*, 1950, **62**, 369), and later elaborated by Huisgen and Krause (*Annalen*, 1951, **574**, 157).



It is possible to distinguish between these two mechanisms by an examination of the effect on the reaction of changes in Ar and in R, of changes of solvent, and of added acids, bases, and salts.

Effect of Nuclear Substituents in the Aryl Group.—The velocities of decomposition of the five compounds $X{\cdot}C_6H_4{\cdot}N(NO){\cdot}CO{\cdot}CH_3$, where X = H, *p*-Me, *p*-Cl, *p*-Br, and *p*-NO_2, have been measured at the four temperatures 20°, 25°, 30°, and 35°. The Arrhenius parameters *B* and *E* are calculated from the first-order rate constants k_1 according to the Arrhenius equation $k_1 = Be^{-E/RT}$. The results are shown in Table 2. In addition, the rates of decomposition of some *meta*-substituted derivatives of nitrosoacetanilide were measured and are given in Table 3. The remarkable insensitivity of the rate of decomposition to changes in the aryl group had been observed by Grieve and Hey (*loc. cit.*), and this is borne out by the measurement of the energies of activation, which are seen to lie within a range of one kcal. that is, almost within the range of experimental error. Thus, the reaction is characterised by the absence of any major resultant effect of changes in Ar.

TABLE 2. *Decomposition of* $X{\cdot}C_6H_4{\cdot}N(NO){\cdot}CO{\cdot}CH_3$ (0·122M) *in benzene.*

X	Temp.	$k_1 \times 10^4$ (sec.$^{-1}$)	k_1 (mean) $\times 10^4$ (sec.$^{-1}$)	E (cal. mole^{-1})	B
H	20°	0·777, 0·775	0·776		$7{\cdot}32 \times 10^{12}$
	25	1·49, 1·51, 1·48	1·49	22,760	$7{\cdot}31 \times 10^{12}$
	30	2·83*, 2·83*	2·83		$7{\cdot}34 \times 10^{12}$
	35	5·17, 5·20	5·185		$7{\cdot}29 \times 10^{12}$
p-Me	20	0·832, 0·832	0·832		$1{\cdot}72 \times 10^{13}$
	25	1·58, 1·57	1·575	23,220	$1{\cdot}67 \times 10^{13}$
	30	3·05*, 3·04*	3·045		$1{\cdot}69 \times 10^{13}$
	35	5·60*, 5·64*	5·62		$1{\cdot}67 \times 10^{13}$
p-Cl	20	0·714, 0·720	0·717		$7{\cdot}52 \times 10^{12}$
	25	1·43*, 1·43*	1·43	22,820	$7{\cdot}75 \times 10^{12}$
	30	2·62, 2·62	2·62		$7{\cdot}52 \times 10^{12}$
	35	4·80, 4·74	4·77		$7{\cdot}40 \times 10^{12}$
p-Br	20	0·733*, 0·745*	0·739		$3{\cdot}33 \times 10^{13}$
	25	1·45*, 1·46*	1·455	23,670	$3{\cdot}33 \times 10^{13}$
	30	2·81*, 2·76*, 2·83*	2·80		$3{\cdot}32 \times 10^{13}$
	35	5·17*, 5·25*	5·21		$3{\cdot}26 \times 10^{13}$
p-NO_2	20	0·989, 0·993	0·991		$3{\cdot}63 \times 10^{13}$
	25	1·85*, 1·85	1·85	23,550	$3{\cdot}44 \times 10^{13}$
	30	3·66*, 3·68*	3·67		$3{\cdot}54 \times 10^{13}$
	35	6·86*, 6·82*	6·84		$3{\cdot}50 \times 10^{13}$

* Velocity constants calculated by Guggenheim's method (see Experimental section).

TABLE 3. *Decomposition of* $X{\cdot}C_6H_4{\cdot}N(NO){\cdot}CO{\cdot}CH_3$ (~0·1M) *in benzene* at 25°.

X	H	*m*-Me	*m*-Cl	*m*-NO_2
$k_1 \times 10^4$ (sec.$^{-1}$)	1·49	1·58	1·62	1·15

The ionic dissociation which is the slow stage of the unimolecular mechanism (*A*) would be thought to be highly sensitive to the presence of substituents in the aryl group, being greatly assisted by electron withdrawal into the aromatic ring, and it is indeed hardly conceivable that such a process should be affected to the exceedingly small extent that is now found. The intramolecular mechanism (*B*), however, has quite different electronic requirements. Whereas electron withdrawal into the aromatic ring facilitates heterolysis of the N–C bond in the same way as dissociation in (*A*), it also has the effect of opposing the $\overset{\curvearrowright}{N{=}O}$ polarisation, the extent of which determines the efficiency of the nitroso-oxygen atom as a nucleophilic reagent. These are two opposing influences, and the direction of the resultant effect is not predictable, being dependent upon the relative importance of the two component effects. The magnitude of the resultant effect, however, must certainly be small.

Effect of Changes in the Acyl Group.—The velocities of decomposition in benzene solution of the five compounds $C_6H_5{\cdot}N(NO){\cdot}CO{\cdot}R$, where R = H, Me, Et, Pr^n, and Pr^i, have been measured over various temperature ranges and the Arrhenius parameters calculated (Table 4). An attempt to complete the series with nitrosopivalanilide (nitrosotrimethylacetanilide, R = CMe_3) failed because the anilide could not be nitrosated, all attempts to do so leading to the formation of a diazonium salt. For purposes of comparison, Table 5 gives the first-order rate constants for the decomposition of these compounds at 25°. Two of these rate constants (*i.e.*, those for R = H and R = Pr^i) were calculated from the Arrhenius parameters given in Table 4. The velocity of decomposition is increased about twelvefold with the introduction of the first methyl group. It then increases progressively, but to a smaller extent, with the introduction of further methyl groups in the α-position, while a methyl group in the β-position has little effect. The energies of activation decrease progressively by about one kcal. for each substituent as the series is ascended. Changes in activation energy are partly compensated by changes in the non-exponental factor, except in the special case of nitrosoformanilide, which has the same non-exponential factor as nitrosoacetanilide. This is reflected in the

TABLE 4. *Decomposition of* C_6H_5·N(NO)·CO·R (0·122M) *in benzene.*

R	Temp.	$k_1 \times 10^4$ (sec.$^{-1}$)	k_1 (mean) $\times 10^4$ (sec.$^{-1}$)	E (cal. mole^{-1})	B
H	40°	0·806, 0·820	0·813		$8·07 \times 10^{12}$
	45	1·51, 1·52	1·515	24,350	$7·93 \times 10^{12}$
	50	2·68, 2·74	2·71		$8·00 \times 10^{12}$
	55	4·76, 4·72	4·74		$8·02 \times 10^{12}$
Me	20	0·777, 0·775	0·776		$7·32 \times 10^{12}$
	25	1·49, 1·51, 1·48	1·49	22,760	$7·31 \times 10^{12}$
	30	2·83, 2·83	2·83		$7·34 \times 10^{12}$
	35	5·17, 5·20	5·185		$7·29 \times 10^{12}$
Et	10	0·654, 0·650	0·652		$1·28 \times 10^{12}$
	15	1·16, 1·17	1·165	21,100	$1·19 \times 10^{12}$
	20	2·34, 2·38	2·36		$1·29 \times 10^{12}$
	25	4·20, 4·30	4·25		$1·26 \times 10^{12}$
Pr^n	10	0·652, 0·660	0·656		$1·53 \times 10^{11}$
	15	1·23, 1·23	1·23	19,900	$1·55 \times 10^{11}$
	20	2·23, 2·20	2·215		$1·55 \times 10^{11}$
	25	3·91, 3·98	3·945		$1·55 \times 10^{11}$
Pr^i	5·5	1·59, 1·59	1·59		$8·19 \times 10^{10}$
	10	2·75, 2·72	2·735	18,760	$8·22 \times 10^{10}$
	15	4·96, 4·74	4·85		$8·17 \times 10^{10}$

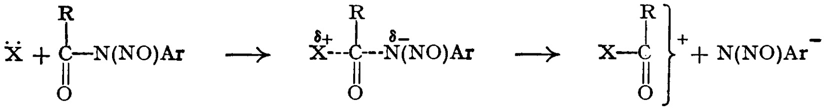
larger difference between the velocities of decomposition of these compounds compared with the corresponding difference for any other pair. A disturbance to the normal sequence of steric factors is perhaps not surprising in this case, because a rather more fundamental alteration in the structure is involved, namely, the introduction of an α-carbon atom.

TABLE 5. *Decomposition of* C_6H_5·N(NO)·CO·R *in benzene at* 25°.

R	H	Me	Et	Pr^n	Pr^i
$k_1 \times 10^4$ (sec.$^{-1}$).........	0·122	1·49	4·25	3·945	14·7

Once again, the significant feature of these results is the *relatively* small magnitude of the effect, rather than its direction. Although, as Huisgen and Krause (*loc. cit.*) point out, the dependence of the rate of rearrangement on the nature of the acyl group is apparently strong, examination of the experimental data shows that it is very much smaller than would be expected for a unimolecular decomposition of type (*A*), but is rather of such a magnitude as is characteristic of bimolecular substitution (S_N2) reactions (Gleave, Hughes, and Ingold, *J.*, 1935, 236). That the direction of the effect is opposite to that generally found in bimolecular substitution reactions is considered to be of little significance, since the analogy between the two reaction types is not close enough to justify any prediction on these grounds alone. In the simpler case of intermolecular deacylation, which is discussed later in this paper, this opposite sequence is indeed found, namely, Pr^i < Et < Me < H.

This reversal of the rate sequence can be seen to arise naturally from the *intramolecular* nature of the rearrangement. The analogy between the intermolecular deacylation



$$\ddot{\text{X}} + \overset{\text{R}}{\underset{\text{O}}{\text{C}}}\text{—N(NO)Ar} \longrightarrow \overset{\delta+}{\text{X}}\text{---}\overset{\text{R}}{\underset{\text{O}}{\text{C}}}\text{---}\overset{\delta-}{\text{N}}\text{(NO)Ar} \longrightarrow \left[\text{X—}\overset{\text{R}}{\underset{\text{O}}{\text{C}}}\right]^{+} + \text{N(NO)Ar}^{-}$$

and the classical picture of bimolecular substitution in an analogous system,

$$\ddot{\text{X}} + \text{R—Y} \longrightarrow \overset{\delta+}{\text{X}}\text{---R---}\overset{\delta-}{\text{Y}} \longrightarrow \text{XR}^{+} + \text{Y}^{-}$$

is close, and the effects of electron-attracting and -repelling substituents in R should follow the same sequence in both reactions. The two effects of electron repulsion, for example, from R are on the one hand to favour the recession of Y, and on the other to inhibit the approach of X. The latter is found to be the dominant effect, and the net result of such a substitution is a *small* reduction in the velocity of the reaction. This is found to be true also for the present intermolecular deacylation.

For the intramolecular rearrangement, however, the sequence is reversed, *i.e.*, $\mathrm{Pr^i} > \mathrm{Et} > \mathrm{Me} > \mathrm{H}$. While the two effects mentioned above still operate there is a third effect of electron repulsion from R, namely, that on the polarisation of the N:O group, the extent of which is increased. This renders the oxygen atom of the nitroso-group more efficient as a nucleophilic reagent as electron repulsion in this direction is increased. Such a factor could very easily be sufficient to reverse the rate sequence found for intermolecular deacylation.

Huisgen and Krause (*loc. cit.*) have advanced an explanation for the reversed rate sequence, which is based on the decreased participation in the resonance hybrid structure of a canonical form in which the N–C bond is double, and consequently rotation about this bond is restricted to a decreasing extent as R becomes increasingly electron-repelling. The present authors consider, however, that such a postulate is unnecessary for the explanation of the experimental data, which are adequately accommodated, as indicated above.

Solvent and Salt Effects.—Grieve and Hey, and Butterworth and Hey (*locc. cit.*), have measured the rates of decomposition of nitrosoacetanilide in a number of solvents and have remarked on the insensitivity of the reaction to the nature of the solvent. The rates of decomposition of nitrosoacetanilide at 25° in ethanol containing various proportions of water, and of lithium chloride, are given in Table 6.

TABLE 6. *Solvent and salt effects on the decomposition of nitrosoacetanilide at* 25°.

Medium	$k_1 \times 10^4$ (sec.$^{-1}$)	Medium	$k_1 \times 10^4$ (sec.$^{-1}$)
Ethanol	1·89	Ethanol + 15% of water	1·76
,, + 5% of water	1·95	,, + 1 equiv. of LiCl	1·85
,, + 10% of water	1·82		

These figures demonstrate the virtual absence of both solvent and primary salt effects. Such a result is quite incompatible with the unimolecular mechanism (*A*), but is easily accommodated by the intramolecular mechanism (*B*), in the transition state of which virtually no separation of charges occurs.

Effect of Added Carboxylic Acids.—The observation was made by Grieve and Hey (*loc. cit.*) that the decomposition of nitrosoacetanilide in acetic acid solution was anomalously slow. Huisgen and Horeld (*loc. cit.*) have reported that this reaction is complicated by an acid-catalysed denitrosation, which results in lower yields of nitrogen. In confirming these results two observations were made. First, the effect is confined to carboxylic acids, acetic anhydride behaving "normally" as a solvent. Secondly, in the decomposition in acetic and propionic acids, marked induction periods appear. These facts are illustrated by the data in Table 7.

TABLE 7. *Decomposition of nitrosoacetanilide at* 25°.

Solvent	$k_1 \times 10^5$ (sec.$^{-1}$)	Induction period (mins.)	Solvent	Added substance	$k_1 \times 10^5$ (sec.$^{-1}$)	Induction period (mins.)
C_6H_6	14·9	0	C_6H_6	Ac_2O (M/6)	15·0	0
Ac_2O	12·4	0	,,	AcOH (M/6)	12·1	28
AcOH	2·51	200	,,	$Et{\cdot}CO_2H$ (M/6)	13·2	15
$Et{\cdot}CO_2H$	2·37	96				

Huisgen and Horeld (*loc. cit.*) have measured the rate of azo-coupling in acetic acid solution, and have shown that in this reaction no retardation occurs. It thus appears that in acetic acid solution the correspondence between the rate of decomposition and that of azo-coupling breaks down. It follows that the effect of the acetic acid on the decomposition must become apparent at a stage in the reaction scheme later than the rearrangement. In a consecutive reaction of this type the first-order law can be strictly obeyed only if one stage is very much slower than any other. The induction period, and the reduced rate, in the present case, therefore indicate the retardation of a stage subsequent to the rearrangement to such an extent that the rates of the two stages become comparable. The probable explanation of this retardation, which is confirmed by work published since these experiments were carried out (de Tar, *loc. cit.*; Huisgen, *Annalen*, 1951, **574**, 184), is that in these solvents the equilibrium (1) lies very much further to the right than it does in benzene and

$$\mathrm{Ar{\cdot}N{=}N{\cdot}O{\cdot}COR} \rightleftharpoons \mathrm{Ar{\cdot}N{\equiv}N^+} + \mathrm{R{\cdot}CO_2^-} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

other comparable solvents, and thus the concentration of the covalent diazo-carboxylate is very much reduced. There is present mainly the diazonium salt, which decomposes slowly, yielding nitrogen and a phenyl ester.

Intermolecular Deacylation.—The oxygen atom of the nitroso-group can be only weakly nucleophilic, so that it should be possible to accomplish an intermolecular deacylation by the introduction of a more powerfully nucleophilic reagent. Thus, if sodium hydroxide or ethoxide is introduced, the evolution of nitrogen becomes extremely rapid. It proceeds, however, at a measurable rate if piperidine is used as the nucleophilic deacylating agent. The deacylation reaction involves the production of an acylpiperidide and the diazo-hydroxide (diazoic acid) (2), which evolves nitrogen rapidly, thus enabling the reaction to be followed:

$$\mathrm{C_6H_5{\cdot}N(NO){\cdot}CO{\cdot}R} + \mathrm{HN{<}C_5H_{10}} \longrightarrow \mathrm{C_6H_5{\cdot}N{:}N{\cdot}OH} + \mathrm{R{\cdot}CO{\cdot}N{<}C_5H_{10}} \quad (2)$$

The three nitrosoacylanilines $\mathrm{C_6H_5{\cdot}N(NO){\cdot}CO{\cdot}R}$, where R = Me, Et, and $\mathrm{Pr^i}$, were allowed to decompose in benzene solution in the presence of an equivalent quantity of piperidine. Under these conditions the reaction of nitrosoformanilide with piperidine was found to be too rapid for convenient measurement. The reaction was found no longer to be of the first order, but to approximate to the second order. Graphs of $1/(a - x)$ against t, where a is the initial concentration of the reactants and x the concentration at time t, gave only fairly good straight lines. The measured rate was shown to be approximately proportional to the concentration of piperidine, and the reaction is of the first order with respect to each reactant. These results are, however, only approximate, because the total yield of nitrogen evolved is reduced by various amounts for the different compounds. With nitroso*iso*butyranilide only about 20% of the theoretical amount of nitrogen was obtained. The nature of the competing side-reaction was established by the isolation of 1-phenyl-3-piperidyltriazen from the reaction of nitroso*iso*butyranilide with piperidine in benzene. The 1-phenyl-3-piperidyltriazen in this solution was also estimated by decomposition with hydrochloric acid, the volume of nitrogen then evolved representing a yield of the triazen of 77·6%. The formation of this triazen in various amounts accounts for the reduced yields of nitrogen evolved from the solutions, and for the only approximate obedience of the second-order law, which is apparent from a simple treatment of the kinetic results.

In order to make a more rigorous analysis, it is necessary to establish the mechanism whereby the triazen is formed. It is probable that the reaction leading to its production is one between diazonium ions and piperidine (3):

$$\mathrm{C_6H_5{\cdot}N_2^+} + \mathrm{HN{<}C_5H_{10}} \longrightarrow \mathrm{C_6H_5{\cdot}N{:}N{\cdot}N{<}C_5H_{10}} + \mathrm{H^+} \quad . \quad . \quad . \quad (3)$$

These diazonium ions may be derived from two sources, first, from the diazo-hydroxide which is formed as a product of reaction (2) and, secondly, from the diazo-ester derived by intramolecular rearrangement of the acylarylnitrosamine. The first of these sources is rendered improbable because if this were true then two molecular proportions of piperidine would be necessary for the production of the triazen. The stoicheiometry of the reaction is in fact such that acylarylnitrosamines react with piperidine in equimolar proportions. The assumption is therefore made that the diazonium ions are derived from the diazo-ester, and that the amount of triazen produced is therefore a measure of the proportion of the acylarylnitrosamine which rearranges intramolecularly. The reaction of diazonium ions with piperidine, like the corresponding reaction with β-naphthol, would be expected to be very much faster than the rearrangement, which would be the rate-determining stage. The reaction would then be of the first order, having the same rate constant as the normal intramolecular rearrangement and the reaction with β-naphthol.

On the basis of these assumptions it is possible to put forward the following reaction scheme, where k_1 and k_2 are first- and second-order velocity constants respectively :

$$\begin{array}{ccccccc} \text{Triazen} & \xleftarrow{k_1} & \text{Nitrosoacylanilide} & + & \text{Piperidine} & \xrightarrow{k_2} & \text{Nitrogen (Acylpiperidine)} \\ (z) & & (a-x) & & (a-x) & & (y) \end{array}$$

Concentrations at time t are given in parentheses. The validity of the above assumptions may be checked by a comparison of values obtained for k_1 from these measurements with those obtained directly. We have

$$\mathrm{d}y/\mathrm{d}t = k_2(a-x)^2 \tag{4}$$

and

$$\mathrm{d}z/\mathrm{d}t = k_1(a-x) \tag{5}$$

and, since $x = y + z$,

$$\mathrm{d}x/\mathrm{d}t = \mathrm{d}y/\mathrm{d}t + \mathrm{d}z/\mathrm{d}t = k_2(a-x)^2 + k_1(a-x) \tag{6}$$

$$= k_2(a-x)(a-x+\alpha)$$

where

$$\alpha = k_1/k_2$$

Thus,

$$k_2\mathrm{d}t = \mathrm{d}x/[(a-x)(a-x+\alpha)]$$

$$= \frac{dx}{\alpha(a-x)} - \frac{dx}{\alpha(a-x+\alpha)}$$

Integration, and determination of the integration constant, give

$$k_2t = \frac{1}{\alpha}\ln\left(\frac{a}{a+\alpha}\right)\left(\frac{a-x+\alpha}{a-x}\right) \tag{7}$$

From equations (4) and (5)

$$\mathrm{d}y/\mathrm{d}z = k_2(a-x)/k_1 = (a-x)/\alpha$$

Now

$$\mathrm{d}z = \mathrm{d}x - \mathrm{d}y$$

Therefore,

$$\mathrm{d}y + (x-a)(\mathrm{d}x - \mathrm{d}y)/\alpha = 0$$

Therefore,

$$\mathrm{d}y - \mathrm{d}x(a-x)/(a-x+\alpha) = 0$$

Integration, and determination of the integration constant, give

$$y = x + \alpha\ln[(a-x+\alpha)/(a+\alpha)] \tag{8}$$

When

$$x = a,\ y = y_\infty,\ \text{and } z = z_\infty$$

then

$$y_\infty = a + \alpha\ln[\alpha/(a+\alpha)]$$

and

$$z_\infty = a - y_\infty = \alpha\ln[(a+\alpha)/\alpha] \tag{9}$$

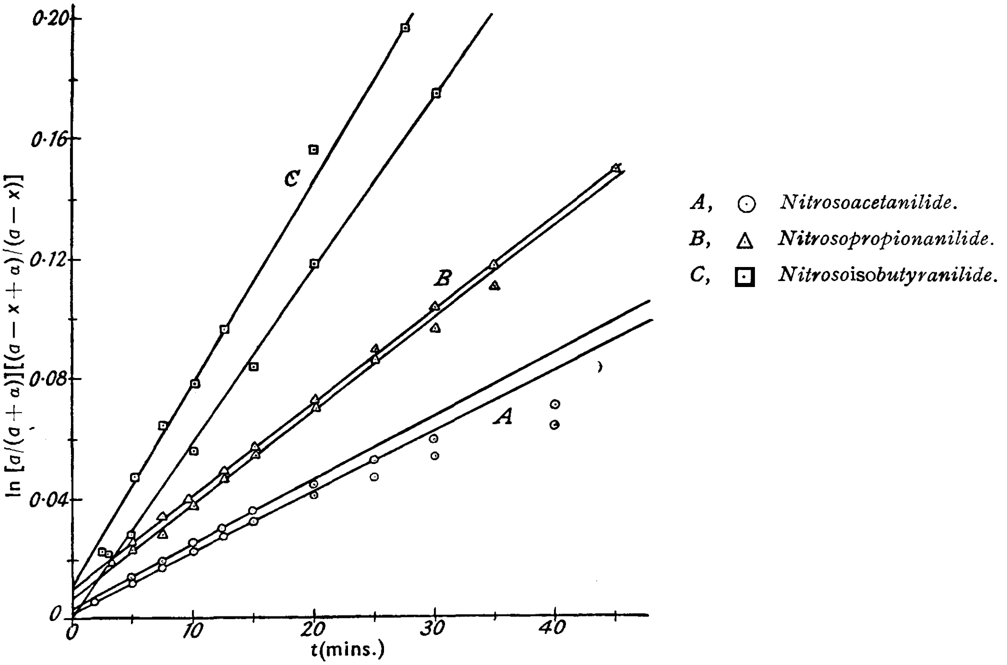
The first- and second-order rate constants k_1 and k_2 may be evaluated graphically, by using equations (7), (8), and (9) in the following manner. The value of α is first determined by a graphical solution of equation (9). With the experimental value of a, calculated values of $z_\infty = \alpha\ln[(a+\alpha)/\alpha]$ are plotted against α, and the value of α corresponding to the experimental value of z_∞ $(= a - y_\infty)$ is read off. With this value for α, the function (8) is plotted, and from this graph the value of x is obtained corresponding to each experimental value of y. With these values of x and α, $\frac{1}{\alpha}\ln\left(\frac{a}{a+\alpha}\right)\left(\frac{a-x+\alpha}{a-x}\right)$ is plotted against t [equation (7)], and k_2 can then be obtained from the slope of this line. Since α is known, this leads also to k_1. These graphs are shown. Good straight lines are obtained for nitrosopropionanilide and nitroso*iso*butyranilide, but some deviation from linearity occurs with nitrosoacetanilide. The first- and second-order rate constants obtained in this manner are given in Table 8.

The values of k_1 agree with those obtained by direct measurement within a factor of 2 in each case. This fact, coupled with the linearity of the graphs shown in the Figure,

TABLE 8. *Reaction of nitrosoacylanilides* $C_6H_5{\cdot}N(NO){\cdot}CO{\cdot}R$ *with piperidine in benzene solution at* 15°.

R	$k_1 \times 10^5$ (sec.$^{-1}$)		$k_2 \times 10^3$ (mole^{-1} sec.$^{-1}$)		α (mean)
Me	7·56	8·06	4·37	4·60	0·017
Et	12·0	11·6	2·93	3·32	0·038
Pr^i	22·4	25·6	0·98	1·42	0·20

indicates that the assumptions made in deriving this analysis are at least approximately correct. The values of k_1 and k_2 illustrate the trends discussed earlier—the intramolecular rearrangement is assisted, whereas the intermolecular deacylation is hindered to a small extent by α-methylation of the alkyl group R, thus supporting the general conception of the reaction which has been developed above.



EXPERIMENTAL

Nitrometry.—The reactions were carried out in reaction vessels of about 30-ml. capacity connected by a short side-arm to 50-ml. nitrometers graduated in 0·2 ml. and containing potassium hydroxide solution in order to absorb any carbon dioxide which may be produced. Velocity constants were calculated in the first instance by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538). In several instances, however, slight deviations from the strict first-order law were found to occur near the beginning of reaction (cf. Huisgen, *loc. cit.*), and an alternative method of calculation was used, the Guggenheim method being somewhat unreliable in such cases. The alternative method was that used by Grieve and Hey (*loc. cit.*) in which $\log V_\infty/(V_\infty - V_t)$ is plotted against t, the first-order velocity constant being given by the slope of this line. Constants which were calculated by the Guggenheim method are marked with an asterisk in the Tables. The solvents used were purified by standard methods, and finally fractionally distilled through a 2-ft., helix-packed column. They were saturated with dry nitrogen immediately before being used for kinetic measurements.

Rates of Azo-coupling.—β-Naphthol was always present in large and constant excess (~0·007M) over the acylarylnitrosamine (~0·00005M). Samples were pipetted into a 1-cm. cell, and the absorption of the solution determined immediately, a Hilger Spekker photoelectric absorptiometer (H.760) with a blue filter (Ilford Series 602) being used. The Beer–Lambert law was obeyed. The intensity I_t of the light passing through the solution at time t was compared with the intensity I_0 of the light passing through the pure solvent, and the extinction $E_t = \log I_0/I_t$ read off directly on the scale of the instrument. The velocity constant was calculated from the slope of the graph of log $E_\infty/(E_\infty - E_t)$ against t, where E_∞ is the extinction of the solution at the end of the reaction. The results are summarised in Table 1.

Nitrosyl Chloride.—Nitrosyl chloride, prepared by Skinner's method (*J. Amer. Chem. Soc.*, 1924, **46**, 737), was dissolved in acetic anhydride to give a 25% solution.

Acylarylnitrosamines.—The acylarylnitrosamines were prepared by the general method of France, Heilbron, and Hey (*J.*, 1940, 369) with slight modifications as indicated in Table 9. The acylarylamine was stirred in acetic acid–acetic anhydride with fused potassium acetate and a little phosphoric oxide. The acetic anhydride solution of nitrosyl chloride was then added dropwise and when the reaction was complete the whole was poured into ice-water, which was stirred vigorously. The acylarylnitrosamine was precipitated, generally as a yellow crystalline solid. Nitrosoacetanilide, nitrosoaceto-*p*-toluidide, nitroso-*p*-bromoacetanilide, and nitroso-*p*-chloroacetanilide (Grieve and Hey, *J.*, 1935, 689), nitroso-*p*-nitroacetanilide (France, Heilbron, and Hey, *loc. cit.*), and nitrosoformanilide (Haworth and Hey, *J.*, 1940, 361) were prepared in this manner. Nitrosoaceto-*m*-toluidide (Grieve and Hey, *loc. cit.*), nitroso-*m*-chloroacetanilide (Huisgen and Krause, *loc. cit.*), and nitroso-*m*-nitroacetanilide (France, Heilbron, and Hey, *loc. cit.*) were unstable oils which tended to decompose rapidly, and hence were essentially unsuitable for kinetic work. They could be isolated by rapid separation and cooling to −80°. As soon as the nitroso-compound melted on slow warming it was poured off any residual ice and acetic acid into benzene. Nitrosopropionanilide (Haworth and Hey, *loc. cit.*) was dried at 0°/2 mm. over potassium hydroxide and phosphoric acid. Nitroso*iso*butyranilide, m. p. 35° (decomp.), and nitroso-*n*-butyranilide, m. p. 39° (decomp.) (Huisgen and Krause, *loc. cit.*), were prepared and dried similarly. They were much less stable and could be kept satisfactorily only below 0°. Details of the preparations are given in Table 9.

TABLE 9. *Nitrosation of acylarylamines with nitrosyl chloride.*

	Solvent, AcOH (%)	Temp.	Time (hrs.)	M. p. (with decomp.)	Yield (%)
Acetanilide	50	5°	½	50°	82
Aceto-*p*-toluidide	50	8	1½	77—78	70
p-Bromoacetanilide	50	8	2½	84—85	64
p-Chloroacetanilide	50	8	2	79—80	70
p-Nitroacetanilide	40	10—12	2½	68—70	74
Aceto-*m*-toluidide	50	8	2	Oil	—
m-Chloroacetanilide ...	50	8	2	Oil	—
m-Nitroacetanilide	40	10—12	1	Oil	—
Formanilide	50	12—15	1	45—46	80
Propionanilide	50	5—7	½	53	82
*iso*Butyranilide	40	0	¼	35	78
n-Butyranilide	40	0	¼	39	80

Isolation of 1-*Phenyl*-3-*piperidyltriazen from the Reaction of Nitroso*isobutyranilide *with Piperidine.*—A solution of nitroso*iso*butyranilide (5·7 g.) and piperidine (2·5 g.) in benzene (200 ml.) was left at room temperature for 2 days. The benzene was removed, and the residue (7·2 g.) was neutralised with aqueous sodium carbonate and extracted with a mixture of benzene and light petroleum (b. p. 60—80°). The extract was passed through a short alumina column, evaporated to dryness, and fractionally distilled. The first fractions consisted mainly of piperidine (b. p. 65—80°/1·5 mm.) and diphenyl (b. p. 95—105°/1·5 mm.), while the last fraction (0·77 g.; b. p. 106°/1·5 mm.) consisted of almost pure 1-phenyl-3-piperidyltriazen. Three recrystallisations from light petroleum yielded yellow crystals, m. p. 42°, which did not depress the m. p. of an authentic specimen prepared by the general method of Elks and Hey (*J.*, 1943, 441).

Estimation of 1-*Phenyl*-3-*piperidyltriazen formed in the Reaction of Nitroso*isobutyranilide *with Piperidine.*—Nitroso*iso*butyranilide (1·17 g.) was warmed in benzene (50 ml.) with piperidine (0·526 g.) in a flask fitted with a reflux condenser, the top of which was connected to a nitrometer. When evolution of nitrogen had ceased, and the nitrometer reading was steady, concentrated hydrochloric acid (2 ml.) was added. The equivalent of 119 ml. of nitrogen measured at S.T.P. was then evolved, corresponding to a yield of 77·6% of 1-phenyl-3-piperidyltriazen, calculated on the nitroso-compound used.

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[*Received, May* 31*st*, 1952.]