# Classical Carbonium Ions. Part 12.[1] The Deamination of 1- and 4-Amino-n-octane

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The deamination products of 1- and 4-amino-octane in acetic acid were examined. The amines were treated with sodium nitrite directly, and also converted into alkylaryltriazenes derived from several arenediazonium cations, which were then acetolysed. *N*-Nitrosobutyramides were acetolysed, and *N*-nitrosoacetamides were butyrolysed, to allow the separate analysis of rearranged and unrearranged products from internal and external nucleophiles. It is concluded that the primary alkylamine is converted by all these different methods in high yield into a primary alkane diazonium ion $RN_2^+$, the properties of which are independent of its method of preparation in that the alkyl cation formed by its decomposition does not capture the leaving group which accompanies its formation, but reacts with solvent to give a constant set of products. The secondary alkylamine behaves differently. Its diazo-derivatives, $RN_2X$, usually undergo effectively concerted decomposition to carbonium ions, nitrogen, and leaving group X. The cations show differing degrees of hydride shift, and capture the internal nucleophile X to a considerable but variable extent, after as well as before rearrangement. The acetolysis of 4-diazo-octane proceeds *via* a much less reactive intermediate, possibly an intimate ion-pair, giving mainly unrearranged 4-acetoxyoctane, plus an olefin

pared and isolated, then solvolysed. The first step in each of these deamination variants has been shown [9,10] to involve the formation of alkyl–$N_2$–X (X = OAc or $\overset{+}{N}H_2$-Ar). The second step might in principle involve either the formation of $RN_2^+$ or, especially if the process

triazenes from benzene- and *p*-nitrobenzene-diazonium tetrafluoroborates and 1-octylamine were prepared; both crystallised, though only the *p*-nitro-compound could be satisfactorily purified, and both reacted rapidly with acetic acid at 25 °C. Finally, 1-octylamine in acetic

amine, the acetolysis of 4-diazo-octane (see below), and of the n-butyrolysis of the 4-(*N*-nitroso-*N*-acetyl) compound ($k$ 2.3 × $10^{-5}$ $s^{-1}$ at 25 °C). A number of points require comment.

(1) Much larger yields of ' internal ' substitution products are obtained in the secondary than in the primary system. For example, in the acetolysis of the nitroso-butyryl amides, the total internal/external (butyrate/acetate) ratios are 13.4/15.5 = 0.86 (secondary) *versus* 2.8/68.3 = 0.04 (primary). In the mirror-image experiment to the former case, in which the nitroso-acetyl s-octyl amide is solvolysed in butyric acid (Table 3), the internal/external (acetate/butyrate) ratio is 1.84, so that the geometric mean of these ratios, 1.26, would be a firm prediction for the internal/external ratio in the case where the two groups were both propionate, labelled so as to be distinguishable. This mean internal/external ratio is perhaps less revealing than the values of 1.25, 1.54, and 0.59 for the internal/external ratios at the 4-, 3-, and 3-positions, respectively. Evidently the advantage of the chemically equivalent internal nucleophile, not at all diminished by one hydride shift, is attenuated by two.

TABLE 3

Internal/external product ratios for nitrosoamide solvolyses

$C_3H_7$–CH($C_4H_9$)N(CO–R)(N=O) ⟶ [$C_3H_7$–CH($C_4H_9$)–N=N–O–CO–R] ⟶ Products

| | | Acetates (%) | | | Butyrates (%) | | | Internal/external | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | R | 2 | 3 | 4 | 2 | 3 | 4 | 2 | 3 | 4 |
| HOAc | $C_3H_7$ | 2.75 | 8.3 | 42.6 | 0.95 | 8.1 | 37.4 | 0.35 | 0.98 | 0.88 |
| HO·CO·$C_3H_7$ | $CH_3$ | 0.72 | 9.7 | 54.4 | 0.73 | 4.0 | 30.5 | 0.99 | 2.43 | 1.78 |
| HO·CO·$C_2H_5$ | $C_2H_5$ | | | | | | | (0.59) | (1.54) | (1.25) |

Results in parentheses are calculated as geometrical means of acetate/butyrate and butyrate/acetate ratios. Yields are normalised such that Σ (acetates + butyrates) = 100%. Solvents were 0.15M in their potassium salt.

(2) The degrees of rearrangement observed in the products formed from different precursors of $R^+$ and solvent vary, in contrast to the virtually constant ratios observed in the primary series. Thus, the 2/4 acetoxy-octane ratio for the *p*-tolyltriazene derived from 4-amino-octane is 0.83/17.2 = 0.048, whereas the *p*-nitrophenyltriazene gives a ratio 1.59/21.8 = 0.073. Indeed, when the log of this ratio, or the 3/4 acetoxy-octane ratio, or the ratio of rearranged octenes (oct-1-ene + oct-2-enes) to unrearranged octenes, is plotted against the σ value for the *para*-substitutent in the set of aryltriazenes, good straight lines are obtained, with slopes of 0.20, 0.13, and 0.12, respectively (correlation coefficients 0.997, 0.969, and 0·999).[2] These slopes correspond to the differences in ρ value for reactions with and without hydride shift, and can be taken as independent measures of the degrees of hydride shift in the cationic intermediate (note that *p*-phenylazo was omitted from these plots, as it behaved as a strongly electron-attracting substituent, presumably because the N=N group is more nearly protonated than in the aqueous reference reaction).

Both these arguments lead to the conclusion that in the overall reaction, $RN_2X$ + HOAc ⟶ ROAc (*etc.*) + $N_2$, the group X is effectively present in the transition states for the product-forming steps when R is secondary alkyl, but not when R is primary alkyl. The difference could be expressed simply in two different ways.

(i) Both reactions could be regarded as two-stage dissociations of $RN_2X$, giving successively $RN_2^+$, then $R^+$, with the difference that when R is primary the intermediate diazonium cation has a high probability (95—99%) of surviving until $X^-$ has diffused away from the encounter pair in which both are initially present, while in the secondary case its chance of doing so is small.

(ii) The two-step dissociation of $RN_2X$ could be an alternative to a concerted decomposition, giving directly $R^+ + N_2 + X^-$, again initially as an encounter-pair. Suppose we assume the activation free energy for the formation of the primary or secondary alkanediazonium ions to be similar, and arbitrarily assume a value higher by 5.4 kJ $mol^{-1}$ for the concerted process in the primary case, and a lower value, by 7.8 kJ $mol^{-1}$, for the concerted process in the secondary case. We would then have concerted/non-concerted ratios of 4 : 96 (primary) and 90 : 10 (secondary). It is easy to see that the product analyses, especially internal/external ratios, quoted above would easily be rationalised. The deduced primary — secondary difference for the free energies of the processes $RN_2^+$ ⟶ $R^+ + N_2$, (5.4 + 7.8) = 13.2 kJ $mol^{-1}$, is only about one quarter of the *ca.* 50 kJ $mol^{-1}$ enthalpy difference between primary and secondary carbonium ions (see following paper). This would fit an early transition state, with very partial formation of the carbocation, in the concerted process. A good general *a priori* argument against concerted processes, that they have unfavourable entropies of activation because of stereoelectronic requirements, may apply very weakly if at all in this instance. The usually disadvantageous enthalpy change associated with complex processes may also be small or negative.[12]

A choice between (i) and (ii) must at this stage be mainly a matter of personal preference in the wielding of Ockam's Razor—does one minimise hypotheses by minimising the number of possible reaction mechanisms or by minimising the numbers of assured intermediates? We prefer explanation (ii) mainly because the extensive work of Grob and his school leaves no doubt that concerted decompositions giving carbonium ions and leaving groups do occur, even when the central molecule also formed, usually an olefin, is much less stable than molecular nitrogen; so reasonable is the hypothesis of

concerted fission, when the carbonium ion formed directly is relatively stable, that we feel the onus of proof should be on those defending the intervention of a very transient s-alkanediazonium cation. We considered, indeed, that this view was implicit in earlier discussions by White *et al.*[9,10] Nevertheless, White and Field [15] have criticised the views expressed in our brief communication,[16] in the light of their work on the decomposition of the tertiary, secondary, and primary butyl *N*-nitrocarbamates in ethanol. We would reply that this is an interesting but different reaction; the alternatives here are decomposition either to $R^+ + N_2O$ or to a species $R{-}N{=}N^+{=}O$, which bears to an alkanediazonium ion the same relationship as an isocyanate bears to an isocyanide. In comparing the concerted decompositions of cyclic azo- and azoxy-compounds to nitrogen and to nitrous oxide, respectively, Snyder *et al.*[17] have found an enormous difference in rate, corresponding to a 200 °C change in reaction temperature. However, we would agree with much that White and Field say,[15] in particular that the two systems, primary and secondary, do not differ qualitatively. On our preferred hypothesis (ii), each undergoes reactions that, to a good approximation, can be regarded as concerted (*i.e.* $X^-$ is present in the final, product-forming transition state) or not. The small yields of RX obtained in the 1-octyl series are still larger than would be expected from intermolecular processes, and must be formed by the capture of an internal nucleophile. Only the ratio of the two rates, concerted: non-concerted, changes from perhaps 90 : 10 (secondary) to, say, 4 : 96 (primary).

In one criticism of our conclusions the Johns Hopkins workers are demonstrably wrong: they comment that the lower proportion of internally derived products in the 1-octyl than in the 4-octyl (*e.g.* of butyrates in the acetolyses of *N*-nitroso-*N*-butyramides) ' is almost certainly a result of the occurrence of a displacement reaction '. But the same difference is apparent (Table 1) when only rearranged products are compared; $S_N2$ displacement by solvent on diazonium ions clearly cannot be made to account for this difference. In their own work the distinction cannot be made, since their use of the 2-butyl system equates rearranged and unrearranged products. Indeed, the only fairly clear comparison that can be made between two sets of experiments which differ in almost every variable possible is between the decomposition of *O*-methyl *N*-butyl-*N*-nitrocarbamate in ethanol, in which the externally derived (ethyl ether) fraction shows much more rearrangement by hydrogen shift from positions 2 and 3 than does the internally derived methyl butyl carbonate fraction, and that of *N*-1-octyl-*N*-nitrosobutyramide in acetic acid, in which (Table 1) there is a small, perhaps insignificant difference in the opposite sense. One explanation could be that the counterion in White and Field's work is the alkyl hydrogencarbonate ion, only weakly hydrogen-bonded to solvent ethanol, the solvent-derived products being obtained mainly by solvent scavenging of dissociated ion-pairs, just as they propose. In our work the much less polar acetic acid would discourage ion-pair dissociation, while the counterion would be $[CH_3CO{\cdot}O \cdots H \cdots O{\cdot}COC_3H_7]^-$, bound by a much stronger hydrogen bond. Assuming a very fast proton-jump within the counterion, both acetate and butyrate would be formed mainly by collapse of the ion-pair. All this, of course, refers only to the small amount of concerted decomposition observed in the primary system.

TABLE 4

Miscellaneous solvolyses of 4-amino-octane derivatives in acetic acid

| | | | | | Acetates [b] | | | Octenes [c] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substrate | Additive | Acetates [a] | Olefins [a] | Amine [a] | 2 | 3 | 4 | 1 | *cis*-2 | *trans*-2 | *cis*-3 | *trans*-3 | *cis*-4 | *trans*-4 | Other products |
| RNH·$N_2$·$C_6H_4$·COMe | 0.1M-$C_6H_5NH_2$ * | 20.6 | 60.9 | 9.8 | 5.0 | 16.9 | 78.1 | (0.4) | 4.4 | 4.6 | 11.2 | 39.3 | 8.7 | 31.5 | <0.3% $RNHC_6H_5$ |
| RNH·$N_2$·$C_6H_4$·COMe | 0.1M-$O_2N{\cdot}C_6H_4{\cdot}NH_2$ * | | | 10.9 | | | | | | | | | | | <0.3% $RNHC_6H_4NO_2$ |
| RNH·$N_2$·$C_6H_4$·COMe | * | 22.6 | 62.0 | 12.4 | 5.2 | 17.0 | 77.8 | 0.4 | 4.3 | 4.6 | 11.1 | 39.5 | 8.3 | 31.7 | |
| RNH·$N_2$·$C_6H_5$ | * | 21.4 | 68.7 | 10.1 | 4.15 | 14.35 | 81.5 | 0.2 | 3.85 | 4.2 | 12.1 | 38.5 | 9.5 | 31.7 | |
| RNH·$N_2$·$C_6H_5$ | 0.5M-$HClO_4$ | | | | 5.0 | 15.9 | 79.1 | 0.4 | 4.0 | 5.0 | 13.1 | 36.6 | 10.4 | 30.5 | |
| RNH·$N_2$·$C_6H_5$ | 0.5M-$NaClO_4$ | | | | 4.8 | 15.0 | 80.2 | 0.4 | 4.0 | 4.7 | 12.4 | 37.7 | 10.1 | 30.8 | |
| RNH·$H_2$·$C_6H_5$ | | | | | 3.85 | 13.8 | 82.4 | | | | | | | | |
| $C_8H_7{\cdot}CN_2{\cdot}C_4H_9$ | * | 16.6 | 12.9 | | 0.10 | 0.60 | 99.3 | | 0.10 | 0.80 | 25.9 | 24.3 | 26.0 | 23.0 | |
| $C_8H_7{\cdot}CN_2{\cdot}C_4H_9$ | 0.5M-$HClO_4$ | 25.6 | 21.5 | | 0.21 | 0.93 | 98.8 | | 0.21 | 1.05 | 24.7 | 24.7 | 25.7 | 23.7 | |
| $C_8H_7{\cdot}CN_2{\cdot}C_4H_9$ | 0.5M-$NaClO_4$ | 23.4 | 18.0 | | 0.13 | 0.91 | 99.0 | | 0.14 | 0.85 | 25.8 | 24.4 | 25.8 | 23.0 | |

[a] Yields, assuming pure starting materials; amine is $C_8H_{17}{\cdot}NHAr$. [b] Normalised to Σ (acetates) = 100. [c] Normalised to Σ (olefins) = 100.
* Containing 0.15M-KOAc.

When 4-diazo-octane was treated with acetic acid, the products were quite different from those obtained from the nitrosoamide solvolysis. This contrasts with the similar products obtained from 1-diazopropane and from the deamination of 1-propylamine,[12] which again imply that in the primary alkyl system the diazonium cation is a good intermediate, living long enough to be reasonably constant in its properties. If the 4-diazonium cation is formed in this reaction, it must give a relatively ' cool ' carbonium ion (as judged by the small degree of hydride shift), and its conformations must be rich in (B) or (C) conformers (see above), since only these can give *cis*-olefins, found to be formed in a *ca.* 1 : 1 ratio with *trans*-isomers, whereas the other precursors give in most cases a ratio nearer 1 : 3, close both to the equilibrium ratio and to that expected from the conformational equilibrium in a $-CH_2{-}\overset{+}{C}H{-}CH_2-$ precursor. If one imagines that protonation of the diazo-compound gives an intimate diazonium ion–acetate ion-pair, which loses nitrogen before it can stereomutate, equilibrate with the diazo-ester, or dissociate as far as the (solvent-separated) ion-pair formed in the other deaminations, both results are explained.

The final, product-forming steps in all these reactions involve some rather general problems, and are dealt with in the following papers.

A number of checks were carried out to verify the unimportance of additives to the reacting solutions. Thus, in the decomposition of 4-diazo-octane, sodium acetate, sodium perchlorate, and perchloric acid all increased the small degree of rearrangement by hydride shift, presumably through the operation of a normal salt effect on solvent polarity. In the decomposition of s-alkylaryltriazenes, addition of other arylamines had little effect, and the foreign arylamine was not alkylated to any detectable extent (<0.3%), suggesting that the formation of the triazene was not significantly reversible within the short timescale of the decomposition. These results are summarised in Table 4. We would also call attention to the need, when the potentially great mechanistic significance of measurements of reaction products in the 0.01—1% yield range is to be exploited, for carefully purified, preferably crystalline substrates to be used, for blank experiments to be carried out, and for chromatographic methods to be checked carefully with known mixtures.

## EXPERIMENTAL

Octan-4-ol was prepared by adding freshly distilled butanal (129 g) in dried ether (200 $cm^3$) with stirring and ice-cooling to n-butylmagnesium bromide, from magnesium (47 g) and n-butyl bromide (270 g) in ether (1 000 $cm^3$), during 35 min. The solution was stirred without cooling for 1 h, then ice-cooling was renewed while aqueous sulphuric acid (800 $cm^3$) was added with stirring. After 1 h water (800 $cm^3$) was added to dissolve the separated solid; the phases were separated and the aqueous layer was extracted with ether (2 × 250 $cm^3$). The ethereal solutions were washed (aqueous $Na_2CO_3$, then aqueous $Na_2S_2O_3$) then concentrated to 1 l and cooled with ice, when a small aqueous layer separated and was removed; after drying ($MgSO_4$) evaporation under reduced pressure and distillation (36 cm Vigreaux column) gave octan-4-ol (178.5 g, 77%, after redistillation of early fractions), b.p. 65—65.5 °C at 10 mmHg, $n_D^{25}$ 1.4228 (Tuot [18] gives b.p. 81 °C at 17 mmHg, $n_D^{20}$ 1.4248). Purity (g.l.c.) was 99.3%.

Octan-4-one was prepared from the alcohol (100 g) in ether (310 $cm^3$), to which was added a solution of technical sodium dichromate (81 g) dissolved in 98% sulphuric acid (108 g) and water (to 420 $cm^3$) with vigorous stirring, during 50 min at 25—35 °C. Stirring was continued for 2 h, then the neutral fraction (92 g) was isolated and found (g.l.c.) to contain 2—3% of alcohol. Phthalic anhydride (5 g) was added, and the mixture was heated to 100 °C for 12 h, then distilled (35 cm Fenske column) giving the ketone (72.7 g, 74%), b.p. 62.0—62.8 °C at 16 mmHg, $n_D^{25}$ 1.4114, now containing 0.25% of octan-4-ol (Asinger *et al.*[19] give b.p. 42 °C at 5 mmHg, $n_D^{20}$ 1.4138). This oxidation is based on the work of Brown and Garg.[20]

4-Hydroxyimino-octane was prepared [21] by adding sodium hydroxide (34.5 g) in water (30 $cm^3$) during 10 min to a stirred mixture of hydroxylamine hydrochloride (59.8 g), octan-4-one (73.6 g) and water (30 $cm^3$) at room temperature, then heating, with continued stirring, for 6 h under reflux. Isolation and distillation (36 cm Vigreaux column) gave the oxime (74.3 g, 90.5%), b.p. 60—62 °C at 0.2 mmHg, $n_D^{25}$ 1.4481 (Asinger *et al.*[19] give b.p. 92 °C at 4 mmHg, $n_D^{20}$ 1.4504).

1-Hydroxyimino-octane was prepared from commercial octanal after redistillation, b.p. 59.6—59.8 °C at 13 mmHg, $n_D^{25}$ 1.4162 (lit.,[19] b.p. 43 °C at 4 mmHg, $n_D^{20}$ 1.4192); to the aldehyde (20 g), hydroxylamine hydrochloride (13.6 g) and water (24 $cm^3$) a solution of anhydrous sodium carbonate (10.6 g) in water (30 $cm^3$) was added at such a rate that the temperature did not exceed 45 °C. After 2 h stirring the solid was collected, then dissolved in ether and dried ($MgSO_4$); evaporation gave a solid (19.1 g) which was crystallised from light petroleum (b.p. 60—80 °C), giving the oxime (13.3 g, 60%), m.p. 59—60.5 °C (lit.,[19] 60 °C).

4-Amino-octane was prepared by a procedure based on that used for 1-aminoheptane; [22] the oxime (74.3 g) in thoroughly dried ethanol (1 100 $cm^3$) was heated to boiling in a flask provided with a Hershberg stirrer and an efficient reflux condenser. Sodium (133 g) was added as rapidly as possible, while the solvent refluxed during cautious external cooling with ice–water. When the addition was complete (1 h) the mixture was cautiously warmed, and more ethanol (100 $cm^3$) was carefully added. When the sodium had dissolved, water (250 $cm^3$) was added and the mixture was distilled into concentrated hydrochloric acid (90 $cm^3$) and water (90 $cm^3$). As distillation proceeded, more water (1 250 $cm^3$) was added, the process becoming one of steam-distillation. The total distillate (2 500 $cm^3$) was concentrated under reduced pressure, and the crude solid hydrochloride was dissolved in the minimum volume of water, which was extracted twice with ether to remove non-basic contaminants. Potassium hydroxide (excess) was added and liberated amine was extracted with ether. The extract was dried ($Na_2SO_4$) and evaporated and the amine distilled (40.6 g, 61%), b.p. 53.7—54.0 °C at 14 mmHg, $n_D^{25}$ 1.4211 (Freylon [23] gives b.p. 64—65 °C at 18 mmHg).

1-Amino-octane was similarly prepared from the corresponding oxime (10 g), b.p. 63.0—63.4 °C at 12 mmHg, $n_D^{25}$ 1.4269 (5.8 g, 64%) (Vogel [24] gives $n_D^{20}$ 1.4292).

4-Acetylamino-octane prepared from 4-amino-octane (2 g, 1 mol) in pyridine (3 $cm^3$) by addition of acetic anhydride (1.1 mol). After 10 min, water (0.5 $cm^3$) was added and the mixture was shaken for 5 min to hydrolyse any anhydride or diacetyloctylamine. Isolation of the neutral fraction gave *4-acetylamino-octane* (76%), m.p. 76—77 °C [from light petroleum b.p. 40—60 °C)] (Found: C, 69.9; H, 12.25. $C_{10}H_{21}NO$ requires C, 70.1; H, 12.35%). Similarly prepared, from 4-amino-octane and butyryl chloride, *4-butyrylamino-octane* crystallised from light petroleum (b.p. 30—40 °C) and had m.p. 30.5—31.5 °C (Found: C, 71.95; H, 12.45; N, 7.1%), while 1-amino-octane and butyryl chloride gave, after crystallisation from light petroleum (b.p. 30—40 °C) *1-butyrylamino-octane*, m.p. 24—25 °C (Found: C, 72.3; H, 12.6; N, 7.15. $C_{12}H_{25}NO$ requires C, 72.3; H, 12.65; N, 7.05%).

*N*-Nitroso-1-butyrylamino-octane was prepared by the method of White,[10d] but with a larger excess of nitrosating agent. The amide (0.4 g) in carbon tetrachloride (3 $cm^3$) was added during 2 min to a stirred suspension prepared by adding recently fused sodium acetate (0.5 g) to carbon tetrachloride (5 $cm^3$) containing nitrogen dioxide (*ca.* 0.5 g) with cooling ($CO_2$–acetone, just cold enough not to freeze the solvent), then bringing to 0 °C. After 30 min at 0 °C the mixture was added to water, and the organic layer was washed (aqueous $Na_2CO_3$), dried ($MgSO_4$) and evaporated

at 0 °C under reduced pressure, when the *nitroso-amide* (**CAUTION**—possible carcinogen!) was obtained as a golden yellow oil in nearly quantitative yield (Found: C, 63.5; H, 10.3; N, 12.5. $C_{12}H_{24}N_2O_2$ requires C, 63.15; H, 10.6; N, 12.25%), $\lambda_{max.}$ (EtOH) 429, 409, 392.5, and 242.5 nm (ε 98, 97.5, 60, and 8 840, respectively), $\nu_{max.}$ ($CCl_4$) 1 508 and 1 730 $cm^{-1}$.

The *N*-nitroso-derivatives of the other two amines were too unstable to survive prolonged evaporation at 0 °C, and were solvolysed without bringing to purity; they showed similar spectroscopic characteristics.

Arenediazonium tetrafluoroborates were prepared by the general method of Roe and Hawkins,[25] from ethyl nitrite (20% excess) added at 0 °C to a stirred solution of the *p*-substituted aniline in 40% tetrafluoroboric acid (400 $cm^3$ $mol^{-1}$) and ethanol (800 $cm^3$ $mol^{-1}$). If after 15 min the salt had not precipitated ether was added. The salt was collected, washed with ice-cold water, alcohol, and ether, then dried *in vacuo*; yields (m.p. [°C], often with decomposition and not always in agreement with literature values) were, for *para*-substituents H, 85% (86.5—88.5); $CH_3$, 45% (97—98); Br, 42% (130—133); $CH_3CO$, 44% (94—95); $C_6H_5N_2$, 69% (143—144); $C_6H_5$, 70% (111—112); $NO_2$, 88% (161). For cases $C_6H_5N_2$ and $C_6H_5$ it was more convenient to diazotise in aqueous ethanolic hydrochloric acid, then precipitate with tetrafluoroboric acid.

Alkylaryltriazenes were prepared by a modification (change of solvent) of the method of White and Scherrer,[9] which in our hands led to easier isolation. A solution or slurry of the arenediazonium tetrafluoroborate (1 mol) in acetonitrile (distilled from $P_4O_{10}$) at 0 °C was added, with stirring and cooling to −10 to −5 °C, to a slurry of amino-octane (1 g, 1.0 mol), anhydrous sodium carbonate (12 g), and acetonitrile (13 $cm^3$) during 10 min. Stirring was continued for 10 min with cooling, then 20 min without cooling. The solid was filtered under vacuum and washed with acetonitrile (3 $cm^3$), then the combined acetonitrile solutions were repeatedly extracted with light petroleum (b.p. 30—40 °C) previously freed from aromatic contaminants. The volume of extractant varied from 30 (*p*-$C_6H_5$) to 150 $cm^3$ (*p*-$NO_2$) according to the polarity of the triazene, divided into 10 or 15 $cm^3$ portions. Light petroleum was removed below 10 °C under reduced pressure. Triazenes derived from 1-amino-octane could be lightened in colour by treatment with charcoal, but this process decomposed those derived from 4-amino-octane. Triazenes which could be crystallised, rather wastefully, from light petroleum at low temperature were: 1-*octyl*-p-*nitrophenyltriazene*, m.p. 80—82 °C (Found: C, 60.85; H, 7.95; N, 19.5. $C_{14}H_{22}N_4O_2$ requires C, 60.4; H, 7.95; N, 20.1%), $\lambda_{max.}$ (iso-octane) 330 nm (ε 22 000); 4-*octyl*-p-*nitrophenyltriazene*, m.p. 54—56 °C, $\lambda_{max.}$ (iso-octane) 333 nm (ε 24 300); 4-*octyl*-p-*phenylazophenyltriazene*, m.p. 52—54 °C (Found: C, 69.05; H, 8.2; N, 19.8. $C_{20}H_{27}N_5$ requires C, 71.2; H, 8.05; N, 20.75%), $\lambda_{max.}$ (iso-octane) 367 nm (ε 28 200); 4-*octyl*-p-*acetylphenyltriazene*, m.p. 76—78 °C (Found: C, 69.75; H, 9.15; N, 15.4. $C_{16}H_{25}N_3O$ requires C, 69.8; H, 9.15; N, 15.25%), $\lambda_{max.}$ 311 nm (ε 23 600). Though liquid at room temperature, both with $n_D^{25}$ 1.5420, 1-*octyl*(*phenyl*)*triazene* and 1-*octyl*-p-*tolyltriazene* were obtained essentially pure; respectively (Found: C, 72.0; H, 9.85; N, 15.65 ($C_{14}H_{23}N_3$ requires C, 72.05; H, 9.95; N, 18.0%), $\lambda_{max.}$ (iso-octane) 273 nm (ε 13 400) (Found: C, 72.2; H, 10.5; N, 17.1. $C_{15}H_{25}N_3$ requires C, 72.8; H, 10.2; N, 17.0%), $\lambda_{max.}$ 277 nm (ε 13 900).

4-Diazo-octane was prepared as previously reported.[26]

*p*-(*N*-*p*-Tolylsulphonylamino)acetophenone was prepared from *p*-aminoacetophenone, toluene-*p*-sulphonyl chloride, and pyridine (71% yield) and had m.p. 204—205 °C; Chattaway [27] reports m.p. 203 °C, but gives no analysis (Found: C, 61.65; H, 5.05; N, 4.85. $C_{15}H_{15}NO_3S$ requires C, 62.25; H, 5.25; N, 4.85%).

p-(N-*Methyl*-N-p-*tolylsulphonylamino*)*acetophenone*, prepared from the above ketone (1 mol), potassium hydroxide (1.1 mol), and methyl iodide (5 mmol) in aqueous t-butyl alcohol (1 : 2, to give a homogenous solution) during 2 days at 25 °C, in 69% yield, had m.p. 103—103.5 °C after recrystallisation from ethanol (Found: C, 63.35; H, 5.7; N, 4.6. $C_{16}H_{17}NO_3S$ requires C, 63.35; H, 5.65; N, 4.6%).

*p*-*N*-Methylaminoacetophenone was obtained, in only 16% yield, by hydrolysis of the foregoing compound in concentrated hydrochloric acid, with stirring and heating under reflux. Isolation of the basic product, two crystallisations from carbon tetrachloride, chromatography on deactivated alumina using ether as eluant, and finally recrystallisation from light petroleum (b.p. 60—80 °C) containing a little ethanol gave the *amino-ketone* as almost colourless prisms, m.p. 107—108 °C (Found: C, 72.55; H, 7.6; N, 9.35. $C_9H_{11}NO$ requires C, 72.45; H, 7.45; N, 9.4%). The literature on this simple compound is surprisingly confused, and we cannot find a satisfactory combination of m.p. and elementary analysis (*e.g.* Lee and Schaffner [28] give m.p. 102—103 °C). Our specimen had $\lambda_{max.}$ (EtOH) 328 nm (ε 24 850), and the expected n.m.r. spectrum.

4-*Methylaminoazobenzene*.—We were unable to obtain this by the method of Miller and Miller,[29] and therefore prepared the corresponding triazene from benzenediazonium tetrafluoroborate (4.0 g, 1.1 mol) in dimethylformamide (10 $cm^3$), which was added to a slurry of anhydrous sodium carbonate (5 g), and redistilled *N*-methylaniline (2 g, 1.0 mol) in dimethylformamide (10 $cm^3$) at 0 °C. After stirring at 20 °C for 40 min water was added, and the mixture was extracted with ether, which was evaporated. More *N*-methylaniline (8 g, 4 mol) and concentrated hydrochloric acid (2 g, 1.0 mol) were added to the residue, and the mixture was heated slowly, with stirring, to 60 °C. Excess of dilute hydrochloric acid was added and the hydrochloride of the desired product separated. Filtration, basification, isolation with ether, and chromatography on alumina (deactivated with 10% by weight of 10% acetic acid; light petroleum–ether as eluant) gave the desired amine as deep orange feathery needles, m.p. 87.5—88.5 °C (from light petroleum) (Miller and Miller [29] give m.p. 88—88.5 °C), $\lambda_{max.}$ (EtOH) 402 nm (ε 28.400), in good agreement with 402 nm (ε 25 700) in 95% ethanol.[30]

Kinetic measurements for nitrosoamides were made at 428 nm with a Unicam SP 800 spectrophotometer, using a 1 cm silica cell fitted with a rubber serum cap pierced by a hypodermic needle, to allow escape of nitrogen, in a thermostatically controlled cell block. The nitrosoamide (25—35 mg) was dissolved in a solution of potassium butyrate in butyric acid or of potassium acetate in acetic acid (*ca.* 5 $cm^3$), and log $[a/(a - x)]$ was plotted manually against time, when a good straight line was observed in each case.

Product analyses involved adding a known weight of substance (triazene or diazo-octane) to 5—10 $cm^3$ of solvent (containing a known quantity of pure n-octane, *trans*-decalin, or both, as internal standard), held at 25 ± 0.1 °C in a thermostatically controlled bath, with stirring. After 30 min, purified light petroleum (b.p. 30—40 °C) was added

and the homogeneous mixture was cooled in ice. An ice-cold stock solution (7 $cm^3$ per $cm^3$ of organic liquid) prepared from potassium hydroxide (134 g), dipotassium orthophosphate (400 g), and water (400 g) was added, with ice cooling. The organic layer was separated (after filtration if necessary), washed twice with cold 1M-sulphuric acid, then water, and used directly for analysis by the methods of ref. 14 (' method B ' for octenes) and for octyl acetates and butyrates. The use of a fore-column permitted the analysis of solutions containing the relatively non-volatile esters at the low column temperatures needed for the olefins, whereas the very volatile hydrocarbons did not interfere with the higher temperature analysis of the esters, so that most of the work reported here was carried out with doubly labelled solutions, the same solvolysis mixture sufficing for all products, except when triazenes were used. In these cases a separate solvolysis mixture was prepared and treated with tripotassium phosphate solution. Thorough extraction with ether, concentration and chromatography on deactivated alumina (typically 100—200 times the weight of substance) gave a series of fractions of which those containing the arylamine were identified by u.v. spectrometry, combined, and made up to a standard volume. The yield was calculated on the assumption that the extinction coefficient was the same as that of a model *N*-methylarylamine. In one case, the mixture of *p*-(*N*-octylamino) acetophenones, the amine (20 mg) from a solvolysis was found to have the expected n.m.r. spectrum. In the case of the alkylation of ' foreign ' amines (Table 4) the analysis, by u.v. spectrophotometry after chromatography was, very approximately, reliable to a factor of 2.

In nitrous acid deamination, the amine (250—350 mg, 1 mol) was dissolved in acetic acid (10 $cm^3$), and powdered sodium nitrite (0.9, 1.0, or 2.0 mol) was added, as evenly as possible, over 30 min with vigorous stirring. The analysis of products was analogous to that for solvolyses. The following experiment emphasised the need to treat the analysis of direct deamination products with caution. A solution of isopropylamine (1 mol) was deaminated in acetic acid labelled with n-octane and *trans*-decalin, as described above, after adding small amounts of octan-4-ol and of its acetate, of oct-1-ene, of *cis*-oct-4-ene and of *trans*-oct-4-ene. Recoveries were: octan-4-ol, 72%; its acetate, 96%; oct-1-ene, 95%; *cis*-oct-4-ene, 58%; *trans*-oct-4-ene, 132%. Octan-4-one could not be detected. The stereomutation of 1,2-disubstituted olefins (' elaidinisation ') is, of course, well known,[31] but is unaccompained by bond migration, so (*cis* + *trans*) sums remain meaningful.

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