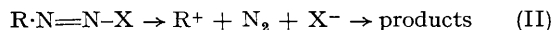
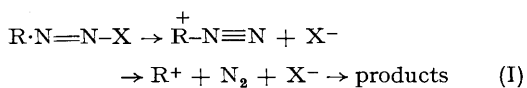


Synchronous Fragmentation in the Deamination of Secondary Carbylamines

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DEAMINATION of 1-propylamine with nitrous acid and some related reactions, in acetic acid and in aqueous dimethylformamide, where shown¹ to give similar ratios of 1- and 2-propyl derivatives, and were therefore believed to involve a common intermediate, the 1-propyldiazonium ion. Otherwise the general acceptance² of a two-stage mechanism (I) (where X = OH, OAc, NH₂Ar, etc.) seems to depend merely on analogy. We have applied two tests to distinguish route (I) from the two-stage mechanism (II). They



differ in that in (II) the R⁺ fragment is liberated close to X⁻, and bears different relationships to X⁻ and to an analogous external nucleophile Y⁻; in (I) diffusion must equate X⁻ and Y⁻. Mechanism (II) was in effect recommended for the decomposition of nitroso-amides derived from cyclohexylamine and α-phenylethylamine in acetic acid,³ for analogous decompositions of alkylaryltriazenes,⁴ and tentatively for the nitrous acid deamination of 2-phenyl-2-butylamine.⁵ In both (I) and (II) ion-pairing of the positive ion would be expected in acetic acid, but diazo-esters and diazonium-carboxylate ion-pairs are in principle distinguishable species even if ionisation is reversible.

We find that for R = 1-octyl, the requirements of mechanism (I) are met to a good approximation in acetic acid (containing 0.15 M-potassium acetate)

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¹ R. Huisgen and Ch. Rüchardt, *Annalen*, 1956, **601**, 1.

² (a) T. A. Geissmann, "Principles of Organic Chemistry", W. H. Freeman, 1962, p. 625, 668; (b) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, 1962, p. 145; (c) *idem, ibid.*, p. 227, 229.

³ E. H. White and C. A. Aufdermarsh, Jr., *J. Amer. Chem. Soc.*, 1961, **83**, 1179.

⁴ E. H. White and H. Sherrer, *Tetrahedron Letters*, 1961, 758.

⁵ D. J. Cram and M. R. V. Sahyun, *J. Amer. Chem. Soc.*, 1963, **85**, 1257.

at 25°. Direct deamination of 1-octylamine, and acetolysis of the *N*-nitrosobutylamide, the phenyltriazenes, and the *p*-nitrophenyltriazenes gave yields of compounds RX, that is, octanols, octyl butyrates, *N*-octylaniline, and *N*-octyl-*p*-nitroanilines, respectively, indicating that capture of an internal nucleophile was unimportant relative to a total yield of substitution products of 68–71%. Furthermore, the four *n*-octyl acetates and six of the seven *n*-octenes were formed in proportions that hardly varied with the internal nucleophile (Table 1). On the other hand, analogous reactions with the 4-octyl derivatives gave much more substantial yields of compounds RX, especially relative to a lower total yield of substitution products (29–44%). The octanols and octyl butyrates were partly rearranged; this argues against a concentrated S_Ni reaction⁶. In the triazene acetolyses, *p*-nitroaniline and aniline were added (1 mol.) as external nucleophiles to the solutions of the *p*-acetylphenyltriazenes, but in neither case were compounds RY formed to a detectable (*ca* 0.5%) extent alongside the *p*-octylaminoacetophenone, RX. Furthermore, product ratios (Table 1 and below) differ significantly, and intelligibly in that the less nucleophilic X is, the more rearrangement. Thus much at least of these reactions must involve the synchronous fragmentation (II); alternatively, the mean lifetime of $RN\equiv N$, appreciable when R = 1-octyl, is short relative to molecular diffusion when R = 4-octyl.

The deamination of substituted cyclohexylamines has been extensively discussed and is

usually^{6b,2c} formulated with diazonium ions as intermediates. Acetolysis of *cis*- and *trans*-*N*¹-4-*t*-butylcyclohexyl-*N*³-phenyltriazenes and its *p*-nitro derivative led to significant yields (Table 2) of alkylanilines and, at least in the axial cases, to significant differences in product-ratios when the aryl residue varied. Here again the synchronous mechanism (II) is important.

The three amines studied are unperturbed secondary carbinylamines having different characteristic conformations. Our conclusions that mechanism (II) is *at least* important in acetic acid can therefore be generalised to other secondary carbinylamines and *a fortiori* to systems related to more stable carbonium ions, that is, to a majority of reported deaminations. Not all theoretical arguments applicable to mechanism (I) extend to (II); for example, activation energies for (II) may be larger than calculated values for (I). As one consequence, for a given secondary system a range of ions of slightly varied "hotness" is available.⁷ Thus, when triazenes, 4-octyl-NH·N₂C₆H₄S, where S = *p*-Me, H, Br, COMe, and NO₂, were acetolysed, good plots for the logarithms of the ratios, 3-acetate/4-acetate, 2-acetate/4-acetate, and rearranged/unrearranged olefins, against σ -values for S were obtained. Slopes were 0.13, 0.20, and 0.12, respectively, corresponding to $\Delta\rho$ for reactions with and without a particular type of rearrangement (correlation coefficients 0.969, 0.997, and 0.999).

Many conclusions implicit in Tables 1 and 2 will be discussed later, but the importance of rearrangements by hydride shift in systems involving secondary carbonium ions requires emphasis.

TABLE 1

Deamination Products from 1- and 4-Amino-octane Derivatives in Acetic Acid

R=	1-Octyl				4-Octyl			
	R·N ₂ OH	R·N ₂ O·COPr	R·N ₂ NHPh	R·N ₂ NHPhNO ₂	R·N ₂ OH	R·N ₂ O·COPr	R·N ₂ NHPh	R·N ₂ NHPhNO ₂
1-acetate	46.0	47.3	46.9	47.7	—	—	—	—
2-acetate	18.5	18.2	16.9	18.5	0.94	0.79	0.89	1.6
3-acetate	2.8	2.6	2.4	2.7	2.4	2.4	3.1	4.8
4-acetate	0.19	0.16	0.15	0.19	30.1	12.3	17.5	21.8
$\Delta 1$	19.5	18.2	20.6	19.6	0.14	0.28	0.15	0.25
t $\Delta 2$	7.7	7.7	7.9	8.1	1.7	3.0	2.9	3.1
c $\Delta 2$	2.1	1.7	2.0	2.0	0.83	2.4	2.6	3.0
t $\Delta 3$	0.95	0.87	0.85	0.88	20.6	28.9	26.3	24.6
c $\Delta 3$	0.52	0.23	0.28	0.29	6.7	7.4	8.3	7.1
t $\Delta 4$	0.08	0.10	0.06	0.04	18.5	23.2	21.7	19.6
c $\Delta 4$	—	—	—	—	6.8	5.9	6.5	5.2
RX	1.8	2.9	1.9	< 0.4	11.3	11.4	10.1	9.0

⁶ (a) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1937, 1252; (b) J. A. Mills, *J. Chem. Soc.*, 1953, 260.

⁷ *cf.* M. S. Silver, *J. Org. Chem.*, 1963, 28, 1686.

TABLE 2

Acetolysis Products from 4-t-Butylcyclohexyl Aryltriazene

	<i>cis</i> -R·N ₂ NHPh	<i>cis</i> -R·N ₂ NHPhNO ₂	<i>trans</i> -R·N ₂ NHPh	<i>trans</i> -R·N ₂ NHPhNO ₂
t4	3.1	3.3	52.4	55.8
c4	3.2	3.4	7.0	8.2
t3	3.3	5.0	0.52	0.48
c3	1.6	2.1	0.33	0.25
t2	—	0.02	0.13	0.18
c2	—	—	0.05	0.04
Δ ⁴	71.0	70.1	13.5	10.7
Δ ³	8.2	8.9	0.48	0.43
Δ ¹	1.4	2.2	—	—
unknown	—	—	1.4	1.5
RX	8.3	5.1	24.2	22.4

All yields are normalised to 100% from total recoveries of *ca* 25% (direct deamination), 55% and 88% (1- and 4-octyl-*N*-nitrosobutyramides), 77—85% (the two *trans*-4-*t*-butylcyclohexylaryltriazenes) or 92—100% (the other six cases). Alkylarylamines were determined spectrophotometrically after adsorption chromatography, all other compounds gas-chromatographically (<4 runs on <2 independent solvolyses). Had 1-*t*-butylcyclohexyl acetate been present (>0.1%) it would have been detected. The unknown hydrocarbon may have been 2-*t*-butylbicyclo[3,1,0]-hexane.

Abbreviations: octyl system, tΔ⁴ = *trans*-oct-4-ene; *t*-butylcyclohexyl system, t4 = *trans*-4-acetate, *etc.*

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