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THE CURTIUS REARRANGEMENT IN AMINIMIDES (II)

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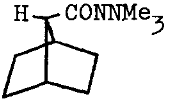
A previous report indicated that the migrating group in the Curtius rearrangement of aminimides (eq. 1) either acquires positive charge or undergoes expansion of groups attached to the migrating carbon atom.[1]

$$\mathrm{RCONNR'_3} \longrightarrow \mathrm{R\text{-}NCO} + \mathrm{NR'_3} \qquad \text{eq. 1}$$

By analogy to solvolysis behavior of 7-norbornenyl systems, if significant carbonium character is involved in the Curtius rearrangement, aminimide 3 should rearrange much faster than 1 or 2 and also rearrange with a greater degree of stereospecificity than 1 due to the expected participation of the π bond in heterolysis of the C_7-CO bond of aminimide 3.[2]


1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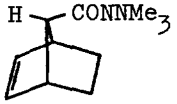
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The structures of aminimides 1 and 3 were determined by nmr spectroscopy and other methods.[3] The isocyanate stereochemistry from the neat thermolysis of each aminimide was determined spectroscopically and otherwise by utilizing the N-substituted acetamide derivative formed by the reaction of the isocyanate with methyl magnesium iodide (eq. 2).[5]

$$\mathrm{RCONNMe_3} \xrightarrow{\text{neat}} \begin{array}{l}\mathrm{RNCO}\\ \mathrm{+NMe_3}\end{array} \xrightarrow[\text{2) } H^+, H_2O]{\text{1) MeMgI}} \mathrm{RNHCOMe} \qquad \text{eq. 2}$$

As shown in Table 1, the relative rates of rearrangement of aminimides 1, 2, and 3 in sulfolane and nitrobenzene are 1:2.2:2.5 and 1:1.8:1.8 respectively and the neat rearrangements of both 1 and 3 proceed with at least 98% retention of configuration. These data indicate that if the migrating group develops carbonium-character, not enough positive charge is generated to trigger significant participation of the double bond in 3 and cause any significant difference in behavior between aminimide 3 and aminimides 1 and 2.

TABLE 1

Kinetic and Product Data of Norbornyl (enyl) Aminimides

$RCONNMe_3$	$k(sec.^{-1})_a$ Sulfolane[a]	$k(sec.^{-1})$ Nitrobenzene[b]	RNHCOMe[c]
syn-7-norbornenyl (1)	$0.65x10^{-4}$ [d]	$3.2x10^{-4}$ [d]	syn-7-norbornenyl (4)
7-norbornyl (2)	$1.4\ x10^{-4}$	$5.6x10^{-4}$	7-norbornyl (5)
anti-7-norbornenyl (3)	$1.6\ x10^{-4}$ [d]	$5.9x10^{-4}$ [d]	anti-7-norbornenyl (6)

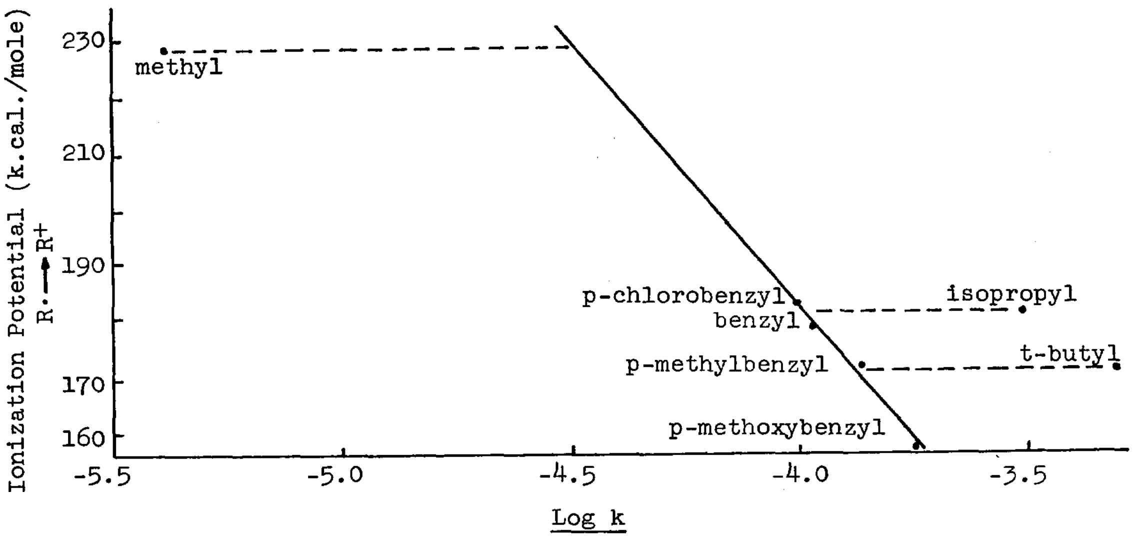
a - Performed at 152.7-153.3° by ampoule method. Loss of carbonyl peak was followed by IR. b - Performed at 154-155° in an nmr spectrometer by following loss of aminimide. c - Each neat thermolysis gave at least 98% of the listed amide after reaction with methyl magnesium iodide. See footnote 5 for structural data. d - Some polymerization occurred but linear first order plots resulted through generally at least one half life.

A substituent study was performed on a series of acyclic aminimides ($RCONNMe_3$) in sulfolane to further study the Curtius rearrangement. A plot of the ionization potential[6] of the radical corresponding to the migrating group (R·) versus the logarithm of the Curtius rate constant[7] is shown in Figure 1.

FIGURE 1

Ionization Potential of R· Versus Log Curtius Rate Constants In Sulfolane at 152.7-153.3°

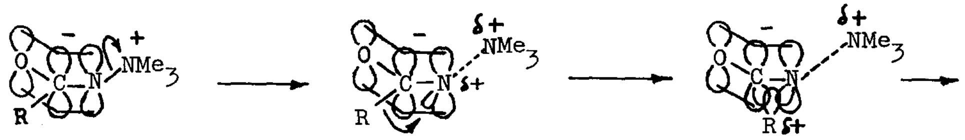
$RCONNMe_3 \longrightarrow RNCO + NMe_3$



The ionization potential of R· measures the energy difference between planar radicals[8] and planar carbonium ions[9] and therefore is a measure of electronic factors only and not of geometric factors. The negative slope of the line through the benzyl series indicates that positive charge is generated on the migrating carbon. In support of this postulate, a sigma-rho plot of the benzyl series utilizing σ^+ gives a rho value of -0.30 with a correlation coefficient of -.997, whereas the utilization of σ gives a very poor correlation. The retarded rate of the Curtius rearrangement in aminimides with the general structure of $ROCONNMe_3$[10] is compatible with the above postulate since the migrating oxygen atom would be less able to accommodate positive charge.

The deviations of the alkyl groups from the line defined by the benzyl series can easily be explained by assuming that expansion of groups attached to the migrating carbon also occurs during the rearrangement. Thus the accelerated rate observed in the t-butyl substituent relative to the benzyl family would be caused by the greater relief of strain involved in the expansion of three methyl groups versus the expansion of a phenyl moeity and two hydrogen atoms.[11] The isopropyl acceleration relative to the benzyl family would obviously not be as great as in the t-butyl case.[11] The benzyl family would be expected to be sterically accelerated over the methyl substituent due to the greater relief of strain involved in the expansion of a phenyl moeity and two hydrogen atoms versus three hydrogen atoms.[11] This interpretation is reinforced by comparing the rates of rearrangement of $RCONNMe_3$ when R was 1-norbornyl or t-butyl as performed in this study.[12] The R group is tertiary in this case but the t-butyl aminimide rearranges 8.3 times faster than the 1-norbornyl case which is consistent with restriction of expansion in this bicyclic system. Thus, plots such as in Figure 1 allow the simultaneous determination of electronic and steric effects.

The observed retention of configuration is compatible with a concerted 1,2 sigmatropic migration to an empty orbital on nitrogen.[13] The Curtius rearrangement has been previously shown to require an anti conformation of the migrating and leaving groups.[14] The migrating group could acquire positive charge in the transition state as a result of bonding to the empty back orbital generated in partial initial heterolysis of the N-N bond. This description would imply that in accommodating the positive charge, the migrating group undergoes partial rehybridization towards sp^2 allowing the attached groups to undergo expansion, thereby causing various rate accelerations.



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2. S. Winstein, Quarterly Reviews, Vol. 23, 141, No. 2 (1969).
3. An isomeric mixture of 7-carbomethoxynorbornenes[4] was reacted with 1,1,1-trimethylhydrazinium iodide to give a mixture of 1 and 3. The nmr spectra were as follows. Compound 1($CDCl_3$): 2,3-H(4.04τ,t), 1,4-H(6.93τ,m), 7-H(7.66τ,m), NMe_3(6.70τ,s). Compound 3($CDCl_3$): 2,3-H(3.97τ,t), 1,4-H(7.07τ,m), 7-H(7.75τ,m), NMe_3(6.68τ,s). The spectra of the known 7-carbomethoxynorbornenes[4] are given for comparison.

syn($CDCl_3$): 2,3-H(4.05τ,t), 1,4-H(6.9τ,m), 7-H(7.7τ,t), OMe(6.5τ,s),
anti($CDCl_3$): 2,3-H(4.00τ,t), 1,4-H(7.0τ,m), 7-H(7.7τ,m), OMe(6.4τ,s). The similar chemical shift variations of the corresponding protons of 1 and 3 with the known syn- and anti-esters are supportive of the assigned structures. Compound 3 had the higher R_f value on silica gel compared to 1 but these values were reversed on silica gel impregnated with 5% silver nitrate which is explicable in terms of the greater complexation ability of the exo double bond. Each aminimide gave the correct elemental analysis.

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5. The nmr spectra of 4, 5, and 6 and the melting points of 5 and 6 were identical to literature values (H. Tanida, et al., J. Org. Chem., 31, 3941 (1966). Furthermore, 4 and 6 could be quantitatively hydrogenated to 5 which further indicated the isomeric nature of 4 and 6.
6. A. Streitwieser, Jr., "Solvolytic Displacement Reactions", p. 181, McGraw-Hill Co., New York, 1962 and A. G. Harrison, et al., J. Am. Chem. Soc., 83, 777 (1961).
7. The rate constants were determined at 152.7-153.3° and represent an average of at least two measurements treated by least squares analyses: t-butyl, 4.78 $(\pm.52)\times10^{-4}$; isopropyl, 3.00$(\pm.05)\times10^{-4}$; methyl, 3.97 $(\pm.52)\times10^{-6}$; p-methoxybenzyl, 1.81 $(\pm.05)\times10^{-4}$; p-methylbenzyl, 1.39 $(\pm.10)\times10^{-4}$; benzyl, 1.06 $(\pm.11)\times10^{-4}$; and p-chlorobenzyl, 0.98 $(\pm.08)\times10^{-4}$. The kinetics were determined by following loss of the carbonyl peak by IR under the assumption that only the Curtius process was operative. The appearance of small, variable peaks in the amide region probably results from reversible dimerization, trimerization and partial hydrolysis (to ureas) of the initially formed isocyanate. The only known alternate primary processes in aminimides are the Stevens (or Wawzonek) rearrangements[15] and self condensation reactions.[16] The specific compounds corresponding to these processes were synthesized where R was methyl or p-chlorobenzyl and were found not to be present in the rearrangement of these aminimides in sulfolane. The neat rearrangement of the isopropyl and t-butyl aminimide gave 100% of the corresponding isocyanate and amine. The rearrangement of the methyl and t-butyl aminimide in water led to an 85% combined yield of the corresponding urea and trimer and 100% yield of urea respectively. The rearrangement of structurally similar aminimides has been reported to give 100% of the Curtius product in nitrobenzene.[1]
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9. G. A. Olah, et al., J. Am. Chem. Soc., 86, 1360 (1964).
10. E. A. Sedor, Tetrahedron Letters, No. 4, 323 (1971).
11. The sum of Taft's E_s values[17] for three methyl groups, two methyl groups and a hydrogen atom, a cyclohexyl group (in substitution of a phenyl group) and two hydrogen atoms, and three hydrogen atoms are 0, 1.24, 1.69, and 3.72 respectively.
12. The rate constants in sulfolane at 152.7-153.3° are 5.6×10^{-5} $sec.^{-1}$ and 4.8×10^{-4} $sec.^{-1}$ for the 1-norbornyl and t-butyl aminimides respectively.
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