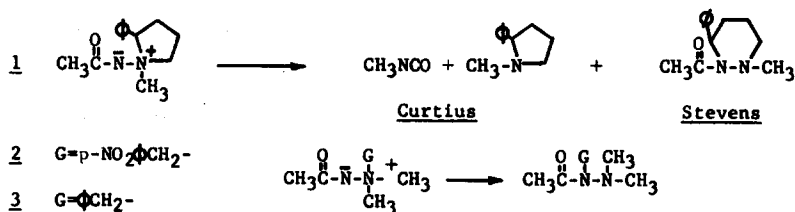


THE CURTIUS REARRANGEMENT IN AMINIMIDES

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The thermal rearrangement of 1-methyl-1-acetyl-imide-2-phenylpyrrolidine (1) yields the Curtius and Stevens products in major and minor yields respectively.¹ However, the Curtius product has not been reported in aminimides with normal N-benzyl substituents. Thus, dimethyl-p-nitrobenzylamine acetimide (2) and dimethylbenzylamine acetimide (3) were reported to yield only the Stevens product in 50% yield upon neat thermolysis.² Moreover, only the Stevens product was reported in the rearrangement of 2 in nitrobenzene.³



The structural dependence of the Curtius and Stevens rearrangements of aminimides, $\text{RCONN}^+(\text{CH}_3)_2\text{CH}_2\text{G}$, in nitrobenzene is shown in Table 1. The Curtius products predominate with increasing size of R to the virtual exclusion of the Stevens product. When R was t-butyl (5) and isopropyl (4), the alkyl isocyanates did not trimerize as is normally the case in the presence of tertiary amines.⁴ When R was methyl (3), the initially formed methyl isocyanate was not detected and a complex reaction mixture resulted. However, the Curtius yield (determined by the production of N,N-dimethylbenzylamine) and the Stevens

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yield from each aminimide summed to 99 + 1% after complete loss of aminimide. No isomerization or elimination of R in the Curtius rearrangement from 4 or 5 was detected. The first order rate constants of the Curtius and Stevens rearrangements were also measured.

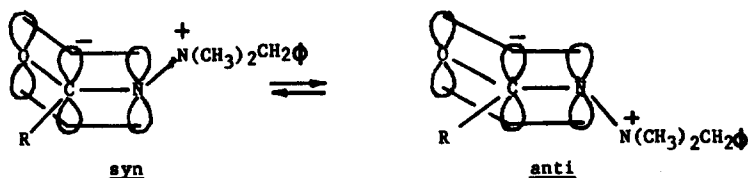
TABLE 1

Thermolysis of $\text{RCONN}^+(\text{CH}_3)_2\text{CH}_2\phi$ in Nitrobenzene^a

R	Curtius Yield (%) ^b	Stevens Yield (%) ^c	k(Curtius) (min. ⁻¹) ^d	k(Stevens) (min. ⁻¹) ^d
CH ₃ (3)	69 ^e	31 ^e	0.013	0.007
(CH ₃) ₂ CH (4)	99	1	0.63	0.007
(CH ₃) ₃ C (5)	99.8	0.2	1.1	—

a - Performed under vacuum in sealed tubes (degassed). b - Absolute yields of N,N-dimethylbenzylamine determined by NMR techniques with an internal standard. c - Absolute yields determined by VPC techniques with an internal standard. d - Relative yields allowed partitioning of the first order loss of aminimides into individual rate constants which were extrapolated to 170° by a plot of ln k vs. 1/T (three temperatures used for each aminimide). e - No significant variation with change in temperature was noted.

Kaplan and Meloy have suggested that the analogous thermal Wolff rearrangement of diazoketones, which exist as a mixture of syn and anti conformers, is derived only from the syn conformer.⁵ This conformer has a desirable anti-periplanar relationship between the migrating and leaving group if the rearrangement is concerted. The imide atom of aminimides is sp² hybridized⁶ and syn, anti exchange has also been detected in trimethylamine acetimide.⁷ An attractive explanation of our results is that 3, 4 and 5 exist as an equilibrium mixture of syn and anti conformers and the greater the steric requirements of R, the greater the population of the syn conformer which would lead to enhanced production of Curtius products.



However, since the syn, anti exchange rate constants are probably very large at 170°⁸ compared to the largest observed Curtius rate constant (1.1 min.⁻¹) at that temperature, the Curtius rate constants should be independent of conformer population. That the Curtius rate constants are independent of conformer populations is evident from inspection of Table 2.

Molecular models of 5 indicate severe steric compression in the anti conformation. The time averaged benzyl resonance of 5 appears at significantly higher field than either 3 or 4.

TABLE 2
Chemical Shifts of $RCONN(CH_3)_2CH_2\phi^a$

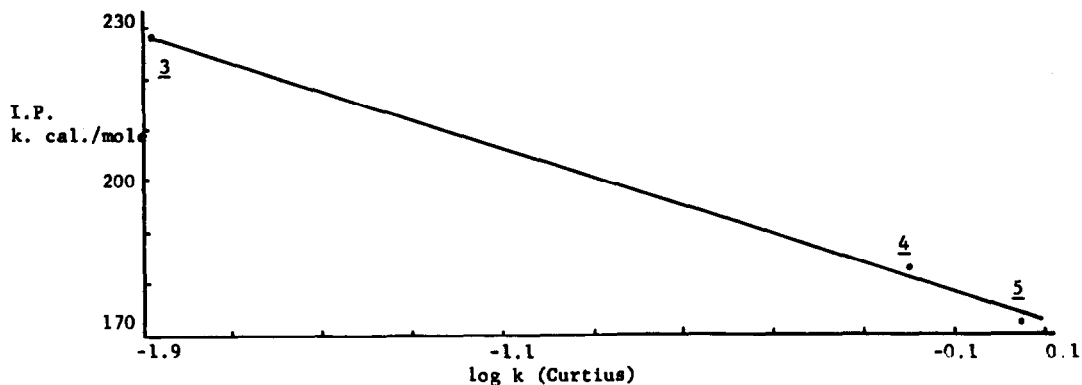
R	$\tau(\text{benzyl methylene})$	$k(\text{Curtius})^b$
CH_3 (3)	5.02	1
$(CH_3)_2CH$ (4)	5.02	49
$(CH_3)_3C$ (5)	5.16	85

a - 10% solutions in $CDCl_3$ at ambient temperature. b - normalized to $k = 1$ for 3.

Therefore, the anti conformer of both 3 and 4 contribute approximately equally and significantly whereas the higher field resonance of 5 originates from a higher proportion of the syn conformer.⁹ Thus, the 49 fold rate increase between 3 and 4 corresponds to a negligible increase in syn conformer population whereas the 1.7 fold increase between 4 and 5 corresponds to a large increase in syn conformer population.

Mechanistic possibilities of the Curtius rearrangement include a migrating group with either radical or carbonium ion character. A diradical mechanism is improbable since products resulting from bromine abstraction were not detected when 4 was decomposed in bromotrichloromethane.¹⁰ However, the data fit well with behavior expected of a migrating group with carbonium character (Figure 1).

FIGURE 1
Ionization Potential^a Versus Log Curtius Rate Constant



a - Energy required to convert an alkyl radical to a carbonium ion.¹¹

The linear dependence of $\log k$ (Curtius) on ionization potential (I.P.)¹¹ indicates

that ΔG^\ddagger is proportional to the energy needed to convert a radical to a carbonium ion. A linear relationship would be expected only if the geometry about the migrating carbon in the transition state were similar to the reactant since I.P. measures the energy difference between planar radicals¹² and planar carbonium ions¹³ (which have identical strain energy). Any flattening of substituents about the central carbon atom would selectively enhance the rates of the more crowded aminimides. A small change in geometry implies that only a small acquisition of charge occurs during the migration, possibly as a result of partial bonding to the migration terminus.

Alternatively, relief of strain about the central carbon atom accompanying a concerted process might be a dominant factor and the three points might fortuitously describe a straight line. Further research concerning these possibilities is currently being conducted.

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8. The analogous syn, anti exchange rates of diazoketones extrapolated to 170° are approximately 10^{+7} min.^{-1.5}
9. In diazoketones, the methine hydrogen (which is cis to the carbonyl group) of the anti conformer absorbs at higher field than in the syn conformer.⁵
10. Isopropyl bromide, propene, or the displacement product of 4 on isopropyl bromide were undetected by vpc and nmr techniques.
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