INTRAMOLECULAR RADICAL TRAPPING IN "SET" RING OPENING OF N-ENOYL AZIRIDINES, A NEW MECHANISTIC PROBE AND A NEW SYNTHESIS OF PYRROLIDONES.

G. Bentz^a, N. Besbes^b, A. Laurent^{*b} and H. Stamm^{*a}

^a Pharmazeutisch-Chemisches Institut, Universität Heidelberg,

Im Neuenheimer Feld 364, D-6900 Heidelberg, Fed. Rep. Germany Laboratoire de Chimie Organique III, Université Claude Bernard Lyon I,

43 Boulevard du 11 Novembre 1918, F-69622 Villeurbanne, France

Summary: N-Acryloyl aziridines 1a-c form pyrrolidones 4a-c via electron attachment, homolytic ring cleavage of the intermediate ketyl, and intramolecular trapping of the radical by the C=C bond of the acryloyl moiety of 1a-c.

Homolytic ring opening of N-acyl aziridines has been established for SET reactions with radical anions 1 of naphthalene (\mathbf{N}^{T}) or anthracene (\mathbf{A}^{T}) and with anthracene hydride (AH)². We report now on a new mechanistic probe for this kind of reaction and on a new synthesis of 3-substituted 2-pyrrolidones.



In a SET initiated reaction sequence of **1a-c** we expected an intramolecular trapping of the intermediate $2^{\overline{}}$ forming the anionic pyrrolidone radical 3. The latter could (a) undergo addition to a partner, (b) undergo disproportionation, (c) abstract a H atom, or (d) accept a second electron yielding the respective dianion 3^{2-} . Our results (Table 1) met this expectation. Reaction (c) was found in run 1-4, reaction (a) occurred in run 7. Reaction (b) was not vet observed. 4b in run 5 may come from reaction (C) as well as (d).

The preceding cyclization is clearly a radical process $(2^{5}\rightarrow 3^{5})$ without

intercurrent reduction of 2^{-1} to its carbanion 2^{2-1} . Considering the amount of reactants in run 1-4 the total yields are too high for two SET steps in the formation of **4a,b**. So, there seems not to be the mechanistic ambiguity of cyclizations known from SET reactions of 5-hexenyl halides³. We assume that in the reactions of **1a-c** there is rather a competition between cyclization and reduction (leading to 5 and 7) than a carbanion cyclization of $2^{2^{-}}$.

By analogy¹, **6b** comes from the anion of **6c**. Reduction of the double bond (6a-c) precedes probably aziridine reduction. The mechanism of the former is unclear although an intermediate dianion of **1b** may be suspected⁴.

R^{1} R^{3} X R^{2}	CH ₂
	AH (AH ⁻ = carbanion)

4a $R^1 = R^2 = X = H$: $R^3 = Ph$ **4b** $R^1 = Me; R^2 = X = H; R^3 = Ph$ **4c** $R^1 = H$; $R^2 = R^3 = Me$; X = AH

Ph-CH=CH-CO-NH-Et 5 Ph-CH2-CH2-CO-NH-R 6a-c **6a** $R = -CH_2 - CHMe_2$ **6b** $R = -CH = CMe_2$ **6c** $R = -CH_2 - CMe = CH_2$ Me₂C=CH-CO-NH-Et 7 Me₂C=CH-CO-NH-CH₂-CH₂-O-CO-Me 8

Table 1. Reactions of 1a-c in THF at room temperature under dry nitrogen.

Run	reactants	M ⁺ ti	me	pyrrolidones ⁵	other products
1	1a, 1.25 eqv. AH	Li ⁺ 5	min	86& 4a	
2	1a, 1 eqv. N ⁻	Na ⁺ 2	đ	56% 4a	14% ^a (28% ^b) 5
3	1b, 1 eqv. AH	Li ⁺ 3	d	69% 4b	
4	1b, 1.25 eqv. AH	Li ⁺ 1	d	78% 4b	
5	1b, 2 eqv. N ⁻	Na ⁺ 6	đ	43% 4b	3% 6a, 5% 6b
6	1c, 1.25 eqv. A	Na ⁺ 10	min	19% ^a (30% ^b) 4c	26% ^a (43% ^b) 7, 1.5% 8^c
7	1c, 7.5 eqv. A.	Na ⁺ 10	min	26% 4c	45% 7

^a Yield calculated from **1**. ^b Yield calculated from consumption of 2 electrons. ^c Formed from unreacted **1c** by guenching the reaction with acetic acid.

REFERENCES

1 H. Stamm, P. Assithianakis, R. Weiß, G. Bentz and B. Buchholz, J. Chem. Soc. Chem. Commun. 1984, 753.

2 H. Stamm, A. Sommer, A. Woderer, W. Wiesert and P. Assithianakis, J. Org. Chem. 50, 4946 (1985).

3 Comp. e. g. the discussion in: F. Garst, J. G. Hines Jr. and J. D. Bruhnke, Tetrahedron Lett. 27, 1963 (1986); E. C. Ashby, T. N. Pham and B. Parks, Tetrahedron Lett. 26, 4691 (1985).

4 H. Stamm, A. Sommer, A. Onistschenko and A. Woderer, J. Org. Chem. 51, 4979 (1986). 5 IR (CH_2Cl_2) v 1700 cm⁻¹; m.p.: **4a**: 104-106°C; **4b**: 155-156°C; **4c**: 212-214°C.

(Received in Germany 19 January 1987)