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STERIC COURSE IN OXIDATIVE RING OPENING OF AZIRIDINE-1-CARBOXYLATES WITH DIMETHYL SULPHOXIDE

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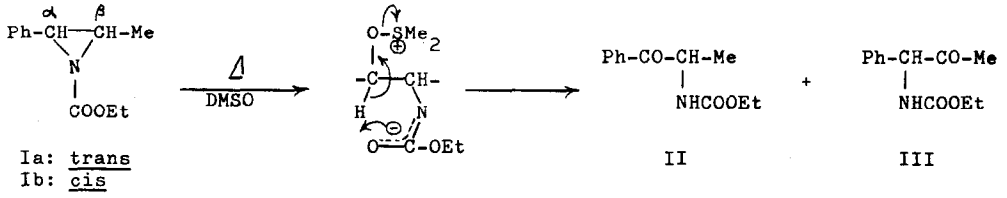
Whereas ring-opening reaction of some 1-aroylaziridines with dimethyl sulphoxide (DMSO) has been reported to give α-aroylaminoketones,[1] the stereochemical aspects have not been described.

Heating of ethyl trans-2-methyl-3-phenylaziridine-1-carboxylate (Ia)[2] in DMSO (120°, 24 hrs.) resulted mainly in N-C_α bond cleavage to afford α-carbethoxyaminopropiophenone (II) along with a small amount of α-carbethoxyamino-α-phenylacetone (III) (82%, II/III = 93:7).[3] Drastically changed product ratio (56%, II/III = 40:60) was observed in rather sluggishly proceeding oxidation (140°, 24 hrs.) of the cis isomer (Ib),[2] which favoured N-C_β bond cleavage. Such dependence of the mode of bond cleavage on the configuration of substrates has previously been recorded for the ring-opening reaction of cis- and trans-2-methyl-3-phenyloxirane.[4] This kind of steric control should originate from the non-bonded interaction between phenyl and methyl group. Though mechanistic details are to be discussed in the future, the key step must involve transfer of proton and removal of dimethyl sulphide as shown below:



Ia: trans
Ib: cis

II III

Towards methyl 2-phenylaziridine-1-carboxylate (IV), the attack of DMSO occurred exclusively on the α-carbon to give α-carbomethoxyaminoacetophenone (V) as a sole isolable product (66%). Aziridines IV were prepared by dehydriodination of methyl N-(2-iodo-1-phenylethane)carbamate (VI), which was in turn obtained by INCO addition to styrene and following treatment with methanol.

This oxidative cleavage seems to constitute a general method for synthesis of α-carbalkoxyaminoketones, since derivatives of aziridine-1-carboxylate are readily available from the corresponding olefins.[2] For instance, 7-carbethoxy-7-azabicyclo[4.1.0]heptane[5] and

9-carbethoxy-9-azabicyclo[6.1.0]nonane (VII) gave α-carbethoxyaminocyclohexanone[6] (65%) and -cyclooctanone (VIII) (48%), respectively. Aziridine VII was synthesized from cyclooctene via the corresponding iodocarbamate IX and/or photolysis of ethyl azidoformate in cyclooctene.

All new compounds II-IX gave correct elemental analyses. The spectral data listed in Table I were consistent with the structures given. Compound II was identical with the authentic specimen prepared by chromic acid oxidation of N-carbethoxypseudonorephedrine.[2]

Table I. Properties and spectrometric data of II-IX

compd.	formula	b.p./mm. [m.p.]	i.r. (cm^{-1})[a]	n.m.r. (τ-value)[b]
II	$C_{12}H_{15}NO_3$	120°/0.04	3350, 1720, 1688	1.9-2.1 (m, 2H), 2.4-2.6 (m, 3H) 4.10 (d, 1H), 4.75 (quintet, 1H), 5.94 (q, 2H), 8.62 (d, 3H), 8.78 (t, 3H)
III	$C_{12}H_{15}NO_3$	[84.8-85.8°]	3340, 1710[c]	2.72 (s, 5H), 3.8-4.1 (broad, 1H), 4.75 (d, 1H), 6.03 (q, 2H), 7.95 (s, 3H), 8.82 (t, 3H)
IV	$C_{10}H_{11}NO_2$	75-80°/0.15	1722	2.82 (s, 5H), 6.37 (s, 3H), 6.63 (q, 1H), 7.45 (d, 1H), 7.87 (d, 1H)
V	$C_{10}H_{11}NO_3$	[97.4-97.8°]	3340, 1726,[c] 1698	1.9-2.1 (m, 2H), 2.3-2.6 (m, 3H), 4.0-4.4 (broad, 1H), 5.30 (d, 2H), 6.26 (s, 3H)[d]
VI	$C_{10}H_{12}INO_2$	[101.6-102.2°]	3275, 1713,[c] 1688	2.65 (s, 5H), 4.4-4.8 (broad, 1H), 5.0-5.3 (m, 1H), 6.30 (s, 3H), 6.48 (d, 2H)[d]
VII	$C_{11}H_{19}NO_2$	103-110°/0.07	1720	5.95 (q, 2H), 7.6-9.1 (m + t, 17H)
VIII	$C_{11}H_{19}NO_3$	110-120°/0.05	3340, 1722 1703	4.2-4.5 (broad, 1H), 5.5-6.2 (m + q, 3H), 7.0-8.5 (m, 12H), 8.75 (t, 3H)
IX	$C_{11}H_{20}INO_2$	[78.5-79°]	3300, 1685[c]	4.6-5.0 (broad, 1H), 5.5-6.2 (m + q, 4H), 7.7-8.4 (m, 12H), 8.75 (t, 3H)

a) Neat unless otherwise stated. b) Determined in CCl_4 at 24°, 60 MHz unless otherwise stated. c)Nujol. d) Determined in $CDCl_3$.

REFERENCES

1) H. W. Heine and T. Newton, Tetrahedron Letters, 1859 (1967).

2) H. Nozaki, Y. Okuyama and S. Fujita, Can. J. Chem., 46, 3333 (1968).

3) The ratios of II/III were determined on the basis of the peak areas of gas chromatograms.

4) H. E. Audier, J. F. Dupin and J. Jullien, Bull. Soc. Chim. France, 2811 (1966).

5) W. Lwowski and T. W. Mattingly, Jr., J. Am. Chem. Soc., 87, 1947 (1965).

6) J. F. W. Keana, S. B. Keana and D. Beetham, J. Org. Chem., 32, 3057 (1967).

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