Tetrahedron Letters No. 26, pp 2339 - 2340, 1978. 0040-4039/78/0622-2339$02.00/0

UNUSUAL RING-CHAIN TAUTOMERISM IN SOME CYCLIC NITRONIC ESTERS

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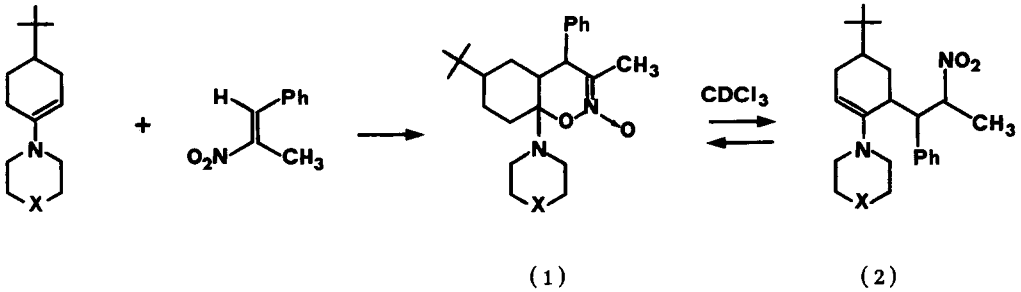
(Received in UK 18 April 1978; accepted for publication 4 May 1978)

Only one case of tautomeric equilibrium between a cyclic nitronic ester and its corresponding open-chain derivative is reported.[1,2] On the contrary, opening of cyclic nitronic esters derived from some non-biased aminocycloalkenes to nitro alkylated enamines is regarded as irreversible.[3]

Anancomeric cyclic nitronic esters (1) were synthesized from 4-*t*-butyl-amino cyclohexenes and 1-phenyl-2-nitropropene (Scheme).

Scheme



X = O, CH_2

P.m.r. studies of (1) in $CDCl_3$ solution indicated that they underwent rapid ring opening to give the trisubstituted enamines (2). However, this conversion was not complete, as the ratio (1):(2) was 1:1 for the morpholino derivative and 2:3 for the piperidino derivative. For the chloroform solution, the same equilibrium mixtures were attained from pure enamines (2). The composition of the equilibrium mixtures was shown to be solvent-dependent. In fact, in benzene and in carbon tetrachloride, these equilibria were so one-sided that only enamines (2) could be detected. However in this case the equilibria were very slow.

These results are of particular interest because reversible formation of an enamine from a heterocyclic compound was not reported so far.

Another aspect which seems deserving to study is the stereochemistry of both heterocycles (1) and enamines (2). Hydrolyses of the former, carried out under kinetic control,[4] led to a ketone which was assigned the less stable *trans* configuration. This result is consistent with a *cis*-fusion between the rings in (1), as already found in other heterocycles derived from biased enamines.[5]

Stereochemical studies of the nitroalkylated enamines (2) seem particularly complex, owing to the presence of chiral carbon atoms and such discussion will form the basis of a later paper.

Some physical and spectroscopic data for the compounds are reported in the Table.

Table

Compound		m.p. °C	i.r. (nujol) cm^{-1}	p.m.r. (CCl_4) δ from TMS
(1)	X=O	112-3	1615 (C=N)	3.6 (m,$C\underline{H}_2OC\underline{H}_2$,$C\underline{H}Ph$, 5H), 2.9 (m,$C\underline{H}_2NC\underline{H}_2$,4H), 2.6 (m,H-4a,1H), 1.7 (d(J=1.5 Hz),$C\underline{H}_3$,3H)
	$X=CH_2$	101-2	1610 (C=N)	3.6 (m,$C\underline{H}Ph$,1H), 2.5 (m,H-4a,1H), 1.7 (d (J=1.5 Hz),$C\underline{H}_3$,3H)
(2)	X=O	127-8	1648 (C=C-N) 1542 (NO_2)	5.5 (m,$C\underline{H}NO_2$,1H), 4.8 (dd,$C=C\underline{H}$,1H), 3.7 (m, $C\underline{H}_2OC\underline{H}_2$,$C\underline{H}Ph$,5H), 1.4 (d (J=6.7 Hz),$C\underline{H}_3$,3H)
	$X=CH_2$	109-10	1646 (C=C-N) 1530 (NO_2)	5.7 (m,$C\underline{H}NO_2$,1H), 4.9 (dd,$C=C\underline{H}$,1H), 3.5 (m, $C\underline{H}Ph$,1H), 1.5 (d (J=6.7 Hz),$C\underline{H}_3$,3H)

Acknowledgement. - This work was supported by C.N.R., Rome.

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[4] Hydroalcoholic solution, pH 6, 5°C. Under less mild conditions, the Nef reaction took place preferentially over hydrolysis.[3]

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