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2+4 Cycloaddition of N-Chlorosulfonylisocyanate to a vinyldihydronaphthalene[1]

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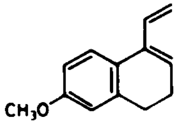
The 2+4 cyclo-addition of chlorosulfonylisocyanate (CSI) and simple dienes[4] proceeds to the energetically favoured formation of carbon-oxygen adducts -δ-iminolactones- although in some cases concomitant carbon-nitrogen[5] addition, leading to δ- lactams, is also observed. The type of product is mainly determined by the intermediate stability of the carboniumion in the dipole[6] 3. No interconversion of the 2+4 CSI-adducts seems to have been reported.

In this communication we describe our results on the addition of CSI 1 to vinyldihydronaphthalene 2, which include a) proof of consecutive formation of both type of adducts, b) determination of the energetics of the conversion-process and c) chemical transformation of the different adducts.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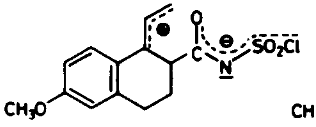
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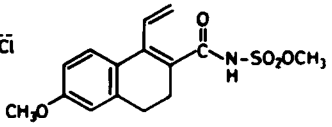
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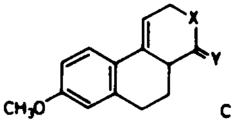
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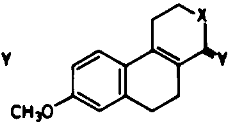
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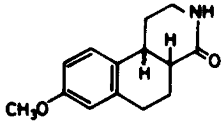
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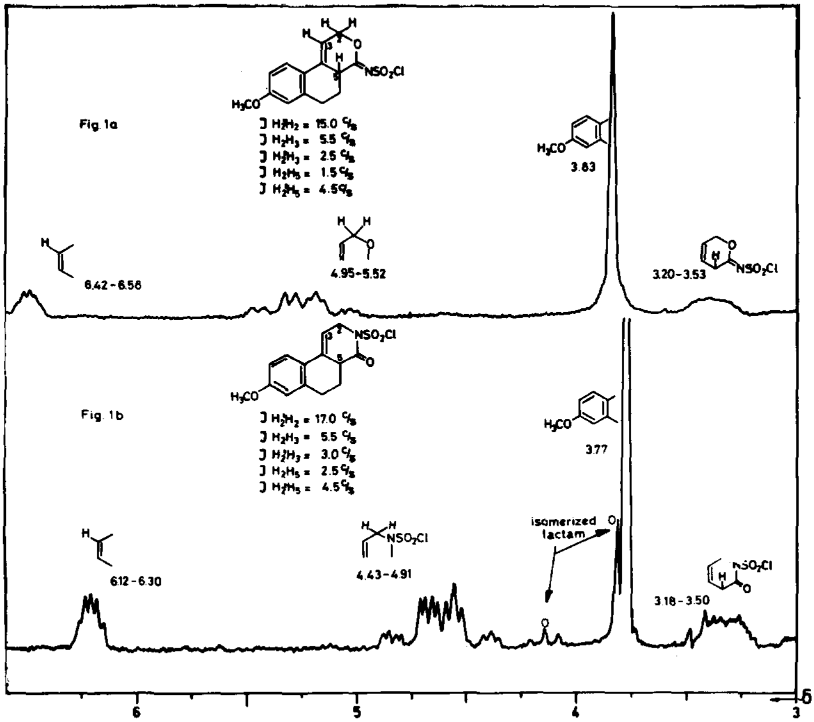
a: X=O Y=NSO$_2$Cl
b: X=NSO$_2$Cl Y=O
c: X=O Y=O
d: X=NH Y=O

Following our interest in the development of new synthetic approaches in the total-synthesis of complex nitrogen-heterocycles[7] 1.0 eq. of the diene 2 was reacted with 1.0 eq. of 1 at -70°C. In a yield of 50% a crystalline adduct A was obtained[8], m.p. 89-91°C (decomp.), μ_D[9] 6.2 D, the NMR-spectrum of which (fig. 1a) was indicative for the formation of a 1:1 adduct[11]. Upon warming of the compound in solution (31°C, $CDCl_3$) a second product B was gradually formed (t½ 29.25 min), NMR-spectrum (fig. 1b). On the basis of the observed chemical shifts and coupling constants most likely structures for A and B are respectively iminolactone 5a and lactam 5b. The direction of addition of 1 to diene 2 is in agreement with a polar intermediate in the transitionstate.

Following the spectral changes at 0°, 16° and 31° in $CHCl_3$, the energy parameters could be calculated on the assumption of a first order reaction occurring. Determination of t½ gave the following values: t½ (0°) 700 ± 20 mn; t½ (16°) 135 ± 3 mn; t½ (31°) 28 ± 2 mn. The corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values[12] then are: $\Delta H^{\ddagger} = 16.6 \pm 1.7$ kcal/mol and $\Delta S^{\ddagger} = -19.6 \pm 2.0$ e.u.

The calculated data could in principle be in agreement with either an isomerization via an open dipolar structure or via a dissociation-recombination process[13]. Concentration[15] and solvent effects[16] will be determined in order to describe the reaction in more detail.



Attempts to isolate lactam 5b in a pure form were not successful, most probably due to its extreme facile isomerization under acidic conditions to the conjugated lactam 6b, the latter being obtained after 8 hr at r.t. in $CDCl_3$ solution: m.p. 160-162°C, μ_D 6.9 D; IR ($CHCl_3$) 1685 cm^{-1}(C=O);NMR($CDCl_3$) δ 3.83 (CH_3O), 4.18 ($C-CH_2-N=SO_2Cl$).

Chemical evidence for the assigned structure has been accumulated from the following series of reactions: Treatment of 5a with NaOMe/MeOH afforded the sulfonester 4: m.p. 99-101°C; IR ($CHCl_3$) 1680 cm^{-1} (C=O),1170 and 1370 cm^{-1} (SO_2OCH_3); NMR ($CDCl_3$) δ 3.80 (CH_3O-Ar), 4.04 (CH_3O-SO_2),5.51 (=CH **trans**, J=20 cps, J=1.5 cps), 5.66 (=CH cis J=11 cps, J=1.5 cps). Hydrolysis of 5a (KI/H_2O) at 0°C under pH adjustment (4-6) gave the corresponding oily δ-lactone 5c, which isomerized to its conjugated isomer 6c:m.p.106-110°C ; IR ($CHCl_3$)1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.82 (CH_3O), 4.47 (CH_2-O-C=O) in quantitative yield upon standing in methanol. On the other hand, treatment of 5b with $NaHCO_3/H_2O$/dioxane (1.5 hr) afforded the lactam 5d: m.p. 178-181°C;IR ($CHCl_3$) 1640 and 1660 cm^{-1} (C=O);NMR ($CDCl_3$) δ 3.78 (CH_3O) δ 4.08 (diffuse)t (C-CH_2-NC=O), sharpens upon D_2O exchange δ 6.08 (=CH);which isomerized to its Δ 8.9-isomer 6d: m.p.172-176°C, IR ($CHCl_3$) 1650 cm^{-1} (C=O) ; NMR ($CDCl_3$) δ 3.51 diffuse triplet (sharpens with D_2O) (CH_2-NC=O), δ 3.81 (CH_3O), upon standing for 16 hr in the dioxane solution. A remarkable fact in the isomerization 5 → 6 is the relative acid sensitivity and base stability of 5b, while the reversal is true for 5d.

Hydrogenation of 5d (10% Pd/C) produced a mixture of saturated lactams 7 (C_4-β-H: C_4-α-H = 1:1); the isomer 6d gave a single hydrogenation product 7 (C_4-β-H), m.p. 161-163°C, IR ($CHCl_3$) 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.76 (CH_3O).

The present investigation confirms the importance of CSI as a synthetic tool in heterocyclic synthesis. Kinetic data thereby confirm the thermodynamic stability of lactam 5b, which constitutes another exception to the generally observed reaction behaviour in CSI (2+4) cycloadditions.

Further conversion of the newly obtained products as well as other reactions of CSI with synthetically important dienes will be reported in due time.

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8. At r.t. or at 0°C difficultly separable reaction mixtures were obtained, consisting of A, B and decomposition products.
9. In order to acquire information on a possible dipolar structure of A and B the dipole moments were determined[10] and compared with the values of structurally related compounds. No exceptional high values were found.
10. R.D.Rapp and J.E.Sturm, J.Chem.Ed. 46, 851 (1969).
11. Under no circumstances could the initial formation of 2 + 2 cycloadducts be demonstrated.
12. A.A. Frost and R.G. Pearson, Kinetics and Mechanism, 2nd ed. page 98, John Wiley and Sons, Inc. New York, London.
13. Compare f.i. the kinetic parameters of the endo→exo isomerization in other 2 + 4 cyclo-adducts.[14]
14. H. Kwart and K. King, Chem.Revs. 68, 415 (1968).
15. The concentrations of 5a used in this work were 0.16 $^{\mathrm{mol}}/\mathrm{l}$ (0°), 0.19 $^{\mathrm{mol}}/\mathrm{l}$ (16°) and 0.18 $^{\mathrm{mol}}/\mathrm{l}$ (31°).
16. Similar effects were observed in different solvents (cf. benzene, diethylether). Kinetic measurements have not been carried out thusfar.