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CONJUGATIVE CYCLOADDITION OF CHLOROSULFONYL ISOCYANATE (CSI) TO VINYLCYCLOPROPANE UNIT IN *spiro*[2.x]ALKANES. NEW PATHWAYS TOWARDS HOMOISOQUINOLINE AND AZA-AZULENE SYSTEMS

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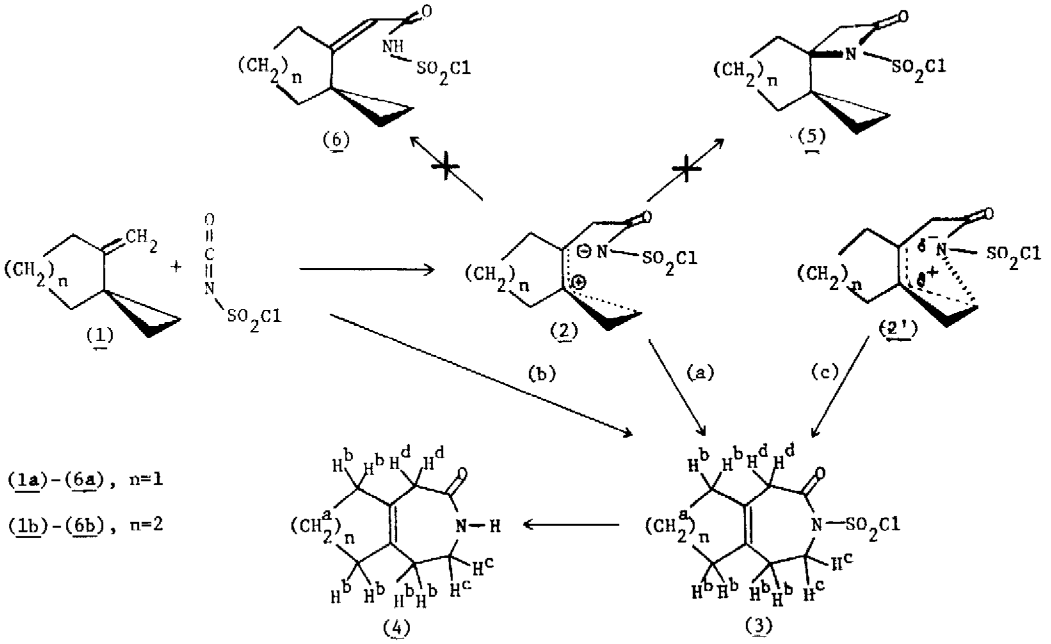
We report here new examples of 7-membered ring lactams,[1] (3a) and (3b), arising from a cycloaddition of CSI to *spiro*-vinylcyclopropanes (1a and 1b) containing the bisected geometry known to provide a highly conjugated system.[2]



4-Methylene-*spiro*[2.x]alkanes (1a and 1b) were exposed to the action of an equimolar quantity of CSI in CH_2Cl_2 solution at -70° and the progress of the reaction was monitored spectrometrically (ir). The formation of (3a) and (3b) was noted to be very fast and no sign of an initial β-lactam formation (1 → 5) or its rearranged product (1 → 6) could be monitored.[3] The 1:1-adduct emerging from the reaction of 4-methylene-*spiro*[2.4]heptane (1a) with CSI analysing as a $C_9H_{12}ClNO_3S$ product (m/e 249) of m.p. 104-5° (49%), was shown to be of structure (3a) : ir (KBr) 1760 cm^{-1}; nmr ($CDCl_3$) spectrum lacking cyclopropane signals and exhibiting τ 8.42 ($2H^a$, m), 8.25-7.20 ($6H^b + 2H^c$, m), 7.23 ($2H^d$, AB, $\Delta\nu$ 21.2 Hz, J 18.8 Hz). Treatment with thiophenol-pyridine in acetone at 0° for 1 hour, followed by column chromatography (florisil), reduced (3a) to (4a). The latter (m.p. 104°) was characterized by its molecular weight 151 (mass spectrometry); ν (KBr) 3160 (N-H) and 1675 cm^{-1} (C=O stretching of large-ring cyclic lactam); and nmr resonances ($CDCl_3$) at τ 8.47 ($2H^a$, m), 8.30-7.70 ($6H^b + 2H^c$, m), 7.56 ($2H^d$, AB, Δν 17.9 Hz, J 17.7 Hz), 2.92 (1H, N-H, which exchanges with D_2O).

Similarly, 4-methylene-*spiro*[2.5]octane (1b) provided the homologous cycloadduct (3b): m.p. 104-5° (28%); ir (KBr) 1765 cm^{-1}; nmr ($CDCl_3$) τ 8.95-7.70 ($4H^a + 6H^b$, m), 7.70-7.38 ($2H^c$, m), 7.49 ($2H^d$, AB, Δν 8.53 Hz, J 18.2 Hz); molecular ion m/e 263 for $[C_{10}H_{14}ClNO_3S]^+$. Reduction of (3b) as before furnished a crystalline 7-membered lactam (4b) with m.p. 94-5°; ir (KBr) absorptions at 3160 (N-H) and 1690 (C=O) cm^{-1}; nmr ($CDCl_3$) at τ 8.97-7.80 ($4H^a + 6H^b + 2H^c$, m), 7.73 ($2H^d$, s), 3.28 (1H, N-H); high resolution ms - 165.11607 for $C_{10}H_{15}NO$ (Calcd. 165.11538).

The addition of CSI to (1) can be viewed as arising from electrophilic attack on the olefin to generate fast equilibrating zwitterionic species (2), being considerably stabilized through homoallylic charge delocalization, which subsequently collapse into homo-Diels-Alder adduct to yield (3) [mode (a)].[4] Alternatively, a concerted mechanism, mode (b) (1 → 3) or a nearly concerted mechanism, mode (c) (1 → 2' → 3), of the symmetry allowed $[2_a + 4_a]$ type should be considered. The ability of cyclopropane to participate as a ${}_{\sigma}2_a$ component in a *concerted reaction is manifested in a* 6_a+2_s *process involving the dienylcyclopropane unit in* homofulvenes and a variety of dienophiles.[5] The participation of CSI as a ${}_{\pi}2_s$ component is not facilitated by either the orthogonal $\pi_{C=O}$ or by the tetrahedral d-$p_{\pi}SO_2Cl$ system, thus the symmetry allowed $[{}_{\pi}4_s + {}_{\pi}2_s]$ addition is not observed in additions of CSI to 1,3-dienes.[6]

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