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THE STEREOSPECIFIC CYCLOADDITION OF CHLOROSULFONYL ISOCYANATE TO CIS- AND TRANS-β-METHYLSTYRENE AND CIS- AND TRANS-3-HEXENE

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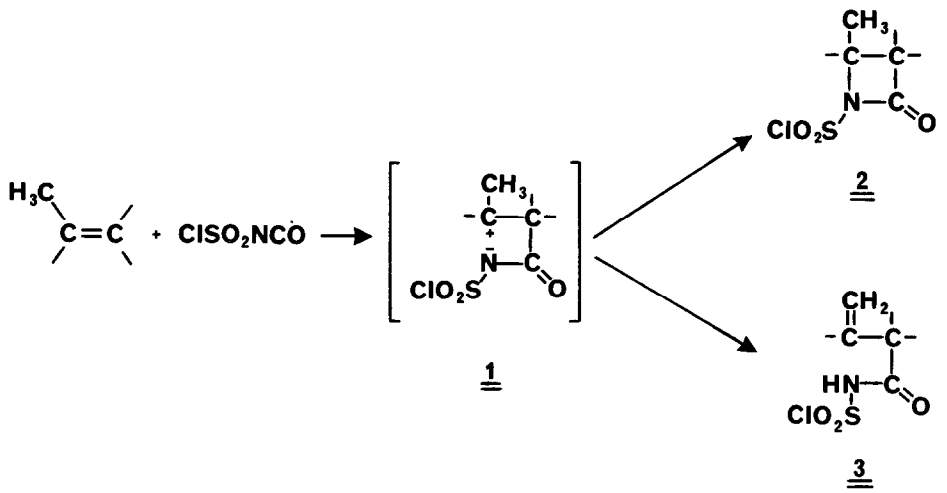
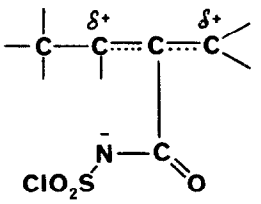
In the cycloaddition of chlorosulfonyl isocyanate (CSI) to olefins, Graf[1,2] envisioned a two-step mechanism involving the initial formation of a 'dipolar adduct' 1 which could stabilize itself through closure to the four-membered 2 and/or via proton shift to 3. Similarly, we suggested for the reaction between CSI and allenes an allyl-type stabilized carbonium ion 4 in the transition state.[3] Most recently we reported the cycloaddition of CSI to bridged



bicyclic (norbornene, norbornadiene and bicyclo[2.2.2]octene) and tricyclic (endo- and exo-dicyclopentadiene) olefins leading, in each case, to a single, unrearranged N-chlorosulfonyl-β-lactam cycloadduct.[4] Since a thermal 2+2 concerted cycloaddition is not allowed by the

Woodward-Hoffman selection rules,[5] we suggested a pseudo-concerted reaction[6] involving the intermediacy of a 1,4-dipole (5) in which the charged species are aligned for bonding.[4]



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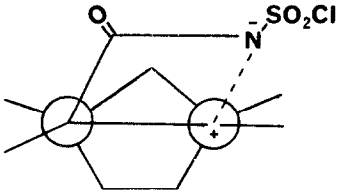

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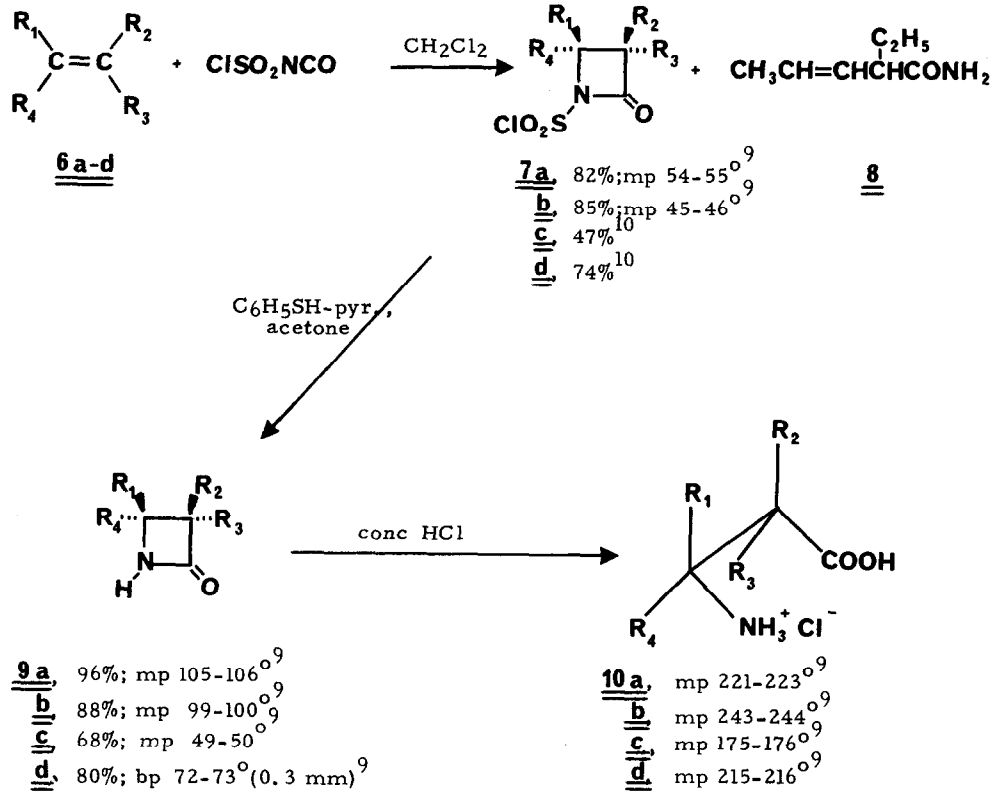
We now wish to report the stereospecific cis-addition of CSI to cis- (6a) and trans-β-methylstyrene (6b) to yield 2+2 cycloadducts, N-chlorosulfonyl-cis- (7a)[9] and -trans-3-methyl-4-phenyl-2-azetidinone (7b),[9] respectively (Scheme I). Similarly, cis-(6c) and trans-3-hexene (6d) led to N-chlorosulfonyl-cis-(7a)[10] and-trans-3,4-diethyl-azetidinone (7d),[10] in addition to small amounts (< 5%) of 2-ethyl-3-pentenamide (8).[9] The retention of configuration of R_1-R_4 in 7a-d is unequivocally supported by nmr data. Thus the eclipsed (dihedral $\measuredangle \cong 0^\circ$) cis-protons in 7a and 7c show the expected vic-coupling of 7.25-7.50 cps while the trans-skewed protons (dihedral $\measuredangle \cong 120^\circ$) in 7b and 7d display vic-coupling of 3.75-4.00 cps. Further, the methyl protons (R_2) in 7a are in the shielding region of the cis-phenyl ring (R_1) and appear as a doublet upfield (0.56 ppm) relative to the trans-methyl protons (R_3) in 7b.[11]

N-Chlorosulfonyl-β-lactams 7a-d were reduced with benzenethiol and pyridine in acetone[1,2] to the appropriate unsubstituted β-lactams, 9a-d. Concentrated hydrochloric acid hydrolysis quantitatively converted 9a and 9b to erythro- (10a)[9] and threo-3-amino-2-methyl-3-phenyl-propanoic acid hydrochloride (10b),[9] respectively, while meso- (10c) and dl-3-amino-2-ethylpentanoic acid hydrochloride (10d)[9] were similarly obtained from 9c and 9d.

The stereoselective cis-addition of CSI to the title compounds eliminate, at least, the intermediacy of 1 enroute to 7a-d. Three mechanisms now seem available to account for the

SCHEME I



6 a-d

7a, 82%; mp 54-55°[9]
b, 85%; mp 45-46°[9]
c, 47%[10]
d, 74%[10]

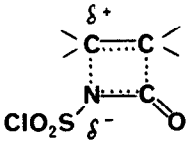
8

9a, 96%; mp 105-106°[9]
b, 88%; mp 99-100°[9]
c, 68%; mp 49-50°
d, 80%; bp 72-73°(0.3 mm)[9]

10a, mp 221-223°[9]
b, mp 243-244°[9]
c, mp 175-176°[9]
d, mp 215-216°[9]

a, $R_1 = C_6H_5$; $R_2 = CH_3$; $R_3 = R_4 = H$
b, $R_1 = C_6H_5$; $R_3 = CH_3$; $R_2 = R_4 = H$
c, $R_1 = R_2 = C_2H_5$; $R_3 = R_4 = H$
d, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$

stereospecificity observed: (i) a pseudo-concerted reaction leading to 5; here one must assume either that the collapse of the internal ion-pair to β-lactam product occurs so rapidly as to preclude rotational isomerism, or that such rotation is hindered by dipolar interaction; (ii) a near-concerted process described by 11;[12] and (iii) a concerted cycloaddition in which case the Woodward-Hoffman rules for thermal 2+2 cycloadditions must be modified for such cumulenic



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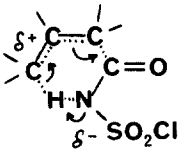

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systems such as CSI perhaps as a consequence of d-orbital participation of the S-atom and/or the lone pair of electrons on the N-atom.[13] Mechanisms i-iii each is probably preceded by a π-complex.[14] Unsaturated amide 8 could be formed via 1 either directly or by the thermally reversible ring-openings of 2 ⇌ 1 → 3,[15] and/or by a concerted addition-elimination involving a cyclic transition state 12.

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