Reaction of Chlorosulfonyl Isocyanate with Aziridines

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The reaction of chlorosulfonyl isocyanate (CSI) with 1,2,3-triphenylaziridine (**1**) and some *cis*- and *trans*-1-cyclohexyl-2-aroyl-3-phenylaziridines, **4-7** and **19-22** has been described. The *cis*-isomers of aziridines, **4-7**, undergo a smooth reaction with CSI to give the corresponding *cis*-isomers of 2-chlorosulfonylimino-1,3-oxazolidines, **8-11**, in good yields (65-67%). While the *trans*-isomers, **19-22**, gave unusual products **23-26** which have been assigned a bicyclic structure, based on their physical and spectral (ir, pmr, ms) data. Plausible mechanisms have been postulated to explain the transformations.

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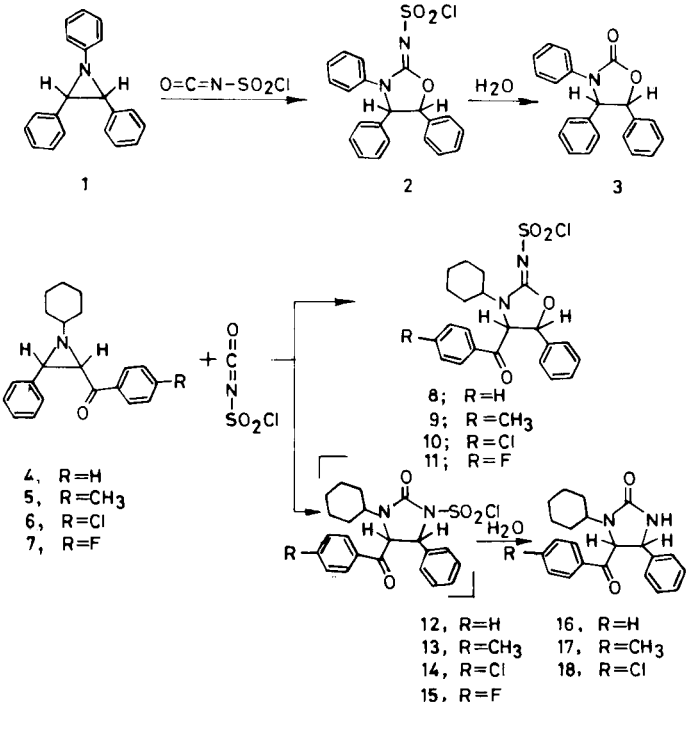
The facile reaction of CSI with various oxiranes, to produce a mixture of 2-chlorosulfonylimino-1,3-dioxolanes and *N*-chlorosulfonyl-1,3-oxazolidin-2-ones, has been reported by us earlier [1]. The reactions of CSI with aziridines form the subject matter of this report. The reaction of unsubstituted aziridines with isocyanates leads to the formation of corresponding urea derivatives [2]. The lithium chloride catalysed reactions of *N*-substituted aziridine with alkyl, acetyl, aryl, aroyl and sulfonyl isocyanates at elevated temperatures (above 100°), however, give 1,3-disubstituted imidazolidin-2-ones [3]. *N*-Substituted aziridines, like epoxides, react readily with CSI, even at low temperatures.

Results and Discussion.

The reaction of *cis*-1,2,3-triphenylaziridine (**1**) with CSI at 0° led to the formation of **2** in 65% yield. The elemental analysis and mass spectral data indicated it to be a 1:1 adduct of **1** and CSI. Its ir spectrum exhibited absorption bands at 1560 (C=N), 1340, 1185 cm^{-1} (SO_2), pointing to the presence of a chlorosulfonylimino moiety. The pmr spectrum of **2** showed an AB quartet (doublets at δ 6.75 (1H) and δ 6.0 (1H, J = 9 Hz) due to adjacent methine protons at C-4 and C-5. The value of the chemical shift of these two protons indicate the formation of a ring expanded product, a five membered oxazolidine ring. The value of coupling constant (9 Hz) is in accordance with the one expected for a 1,3-oxazolidine system with *cis*-orientation of hydrogens at C-4 and C-5 [4]. The above data support the structure assigned to **2**, *viz.* *cis*-2-chlorosulfonylimino-3,4,5-triphenyl-1,3-oxazolidine. This structural assignment was further confirmed by converting **2** to the corresponding 1,3-oxazolidin-2-one derivative **3** by a mild hydrolysis. The compound **3** showed the expected carboxyl absorption at 1730 cm^{-1} in its ir spectrum. Besides, the melting point of this compound is in good agreement with the value reported in the literature [5].

SCHEME 1



cis-1-Cyclohexyl-2-aroyl-3-phenylaziridines **4-7** reacted with CSI in an analogous manner. The reaction of **4** with CSI affords **8** in 72% yield, which precipitates out from the reaction mixture (leaving behind another component **12** in the mother liquor). The compound **8** has similar physical and spectral characteristics as that of **2**. Its ir spectrum exhibited an absorption band at 1675 cm^{-1} indicating that the benzoyl carbonyl remains intact during the reaction. The pmr spectrum showed a pair of doublets, due to the adjacent methine protons at C-4 and C-5, at δ 6.14 and δ 5.93 with a coupling constant J = 9 Hz. This indicates the *cis*-stereochemistry around C-4 and C-5 and the stereospecific nature of the reaction. Thus on the basis of its physical and spectral data **8** was assigned the structure as *cis*-2-chlorosulfonylimino-3-cyclohexyl-4-benzoyl-5-phenyl-1,3-oxazolidine. The other possible regio-isomeric (4-phenyl) structure for **8** was not favoured based on the mass spectral data of **9-11**. All these compounds, **9-11**, showed a common, prominent mass peak at m/e 105, indi-

Table 1

Physical Data of 2-Chlorosulfonylimino-1,3-oxazolidines **2**, **8-11** and 1,3-Imidazolidin-2-ones **16-18**

Compound No.	Mp (°C)	Yield (%)	Formula	Analysis % Calcd. C	H	N	Found C	H	N
2	138-139	66	$C_{21}H_{17}ClN_2O_3S$	61.10	4.12	6.79	61.23	4.02	6.85
8	180-182	67	$C_{22}H_{23}ClN_2O_4S$	59.14	5.15	6.27	58.95	5.24	6.41
9	187-188	67	$C_{23}H_{25}ClN_2O_4S$	59.95	5.43	6.08	59.81	5.49	6.15
10	168-169	67	$C_{22}H_{22}Cl_2N_2O_4S$	54.90	4.57	5.82	54.71	4.68	5.94
11	166-167	66	$C_{22}H_{22}FClN_2O_4S$	56.84	4.74	6.03	56.89	4.64	6.14
16	188-189	19	$C_{22}H_{24}N_2O_2$	75.86	6.90	8.04	75.72	6.81	8.22
17	193-195	18	$C_{23}H_{26}N_2O_2$	76.24	7.18	7.73	76.08	7.02	7.82
18	214-215	18	$C_{22}H_{23}ClN_2O_2$	69.04	6.01	7.32	69.21	6.16	7.23

Table 2

IR, PMR and Mass Spectral Data of 2-Chlorosulfonylimino-1,3-oxazolidines **2**, **8-11** and 1,3-Imidazolidin-2-ones **16-18**

Compound No.	IR Spectra, cm^{-1} (potassium bromide)	PMR Spectra, δ (deuteriochloroform)	Mass Spectra m/e (relative intensity)
2	1560 (C=N), 1340, 1185 (SO_2)	7.1-7.7 (m, 15H, aromatic), 6.75 (d, 1H, J = 9 Hz, C-5H), 6.0 (d, 1H, J = 9 Hz, C-4H)	412 (M^+, 4), 411 (M^+-1, 9.5), 376 [(M^+-1)-Cl, 5], 312 [(M^+-1)-SO_2Cl, 6], 270 (10), 207 (10), 180 (100), 105 (15), 77 (40)
8	1675 (C=O), 1585 (C=N), 1340, 1170 (SO_2)	7.0-7.4 (m, 10H, aromatic), 6.14 (d, 1H, J = 9 Hz, C-5H), 5.83 (d, 1H, J = 9 Hz, C-4H), 3.7-3.9 (m, 1H, *N*-cyclohexyl C-H), 1.0- 2.2 (m, 10H, cyclohexyl CH_2)	446 (M^+, 0.4), 445 (M^+-1, 0.4), 411 (M^+-Cl, 1.1), 410 (4), 341 (10), 330 (3), 305 (3), 243 (10), 118 (35), 105 (100), 91 (15), 83 (20), 77 (38), 64 (20)
9	1680 (C=O), 1590 (C=N), 1342, 1175 (SO_2)	7.0-7.35 (m, 9H, aromatic), 6.14 (d, 1H, J = 9 Hz, C-5H), 5.7 (d, 1H, J = 9 Hz, C-4H), 3.7-3.9 (m, 1H, *N*-cyclohexyl C-H), 2.25 (s, 3H, CH_3), 1.0-2.0 (m, 10H, cyclohexyl CH_2)	460 (M^+, 0.3), 339 (40), 250 (40), 204 (20), 160 (100), 119 ($CH_3C_6H_4CO^+$, 50), 106 ($C_6H_5CHO^+$, 60), 105 ($C_6H_5CO^+$, 55), 91 (30), 83 (15), 77 (70), 64 (30)
10	1685 (C=O), 1590 (C=N), 1350, 1175 (SO_2)	7.0-7.4 (m, 9H, aromatic), 6.1 (d, 1H, J = 9 Hz, C_5-H), 5.65 (d, 1H, J = 9 Hz, C_4-H), 3.75-3.95 (m, 1H, *N*-cyclohexyl C-H), 1.05-2.25 (m, 1H, cyclohexyl CH_2)	480 (M^+, 0.4), 445 (M^+-Cl, 3), 380 [(M^+-1)-SO_2Cl, 0.5], 364 (6), 343 (15), 341 (20), 261 (20), 259 (40), 223 (20), 161 (30), 139 (100), 118 (40), 111 (35), 105 (20), 91 (30), 83 (30), 77 (20), 64 (30)
11	1680 (C=O), 1585 (C=N), 1345, 1170 (SO_2)	7.1-7.5 (m, 9H, aromatic), 6.2 (d, 1H, J = 9 Hz, C-5H), 5.6 (d, 1H, J = 9 Hz, C_4-H) 3.7-4.0 (m, 1H, *N*-cyclohexyl C-H), 1.1-2.1 (m, 10H, cyclohexyl CH_2)	464 (M^+, 0.5), 429 (M^+-Cl, 1), 365 [(M^+-SO_2Cl, 2)], 341 (M^+-FC_6H_4CO, 15), 243 (10), 161 (40), 123 ($FC_6H_4CO^+$, 100), 118 (30), 105 ($C_6H_5CO^+$, 10), 95 (10), 91 (5), 77 (10), 64 (15)
16	1650, 1710 [b] (C=O), 3200 (NH)	7.0-7.6 (m, 10H, aromatic), 5.55 (d, 1H, C-4H), 5.20 (d, 1H, C-5H), 4.70 (s, 1H, NH [a]), 3.6-3.9 (m, 1H, *N*-cyclohexyl C-H), 1.2-1.8 (m, 10H, cyclohexyl -CH_2-)	348 (M^+, 0.5), 243 (M^+-C_6H_5CO, 65), 161 (100), 118 (35), 105 (25), 91 (20), 77 (28)
17	1675 (C=O), 3200 (NH)	7.0-7.6 (m, 9H, aromatic), 5.55 (d, 1H, C-4H), 5.20 (d, 1H, C-5H), 4.70 (bs, 1H, NH [a], 3.65-3.95 (m, 1H, cyclohexyl C-H) 1.70 (s, 3H, CH_3), 1.2-1.8 (m, 10H, cyclohexyl (CH_2))	362 (M^+, 0.1), 243 (M^+-$CH_3C_6H_4CO$, 90), 161 (85), 118 (100), 119 (25), 105 (50), 91 (68), 83 (20), 77 (85)
18	1660 (C=O), 3200, 3050 (NH)	7.0-7.7 (m, 9H, aromatic), 5.50 (d, 1H, C-4H), 5.25 (d, 1H, C-5H), 4.70 (bs, 1H, NH [a]), 3.65-3.9 (m, 1H, *N*-cyclohexyl C-H), 1.1-2.0 (m, 10H, cyclohexyl CH_2)	382 (M^+, 0.3), 243 (60), 161 (100), 139 (35), 118 (60), 111 (20), 83 (20), 77 (70)

[a] Exchangeable with deuterium oxide. [b] In carbon tetrachloride solution.

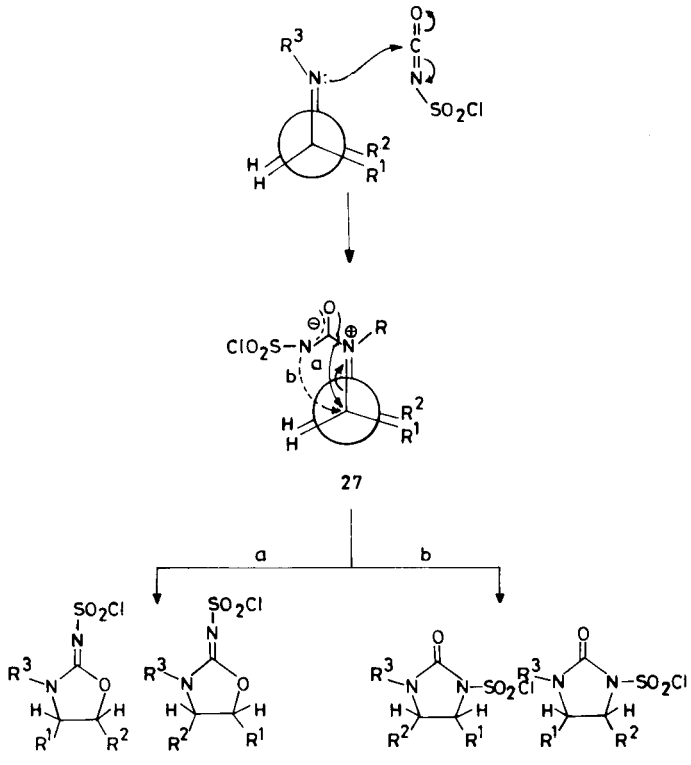
cating the presence of a benzoyl ion fragmet. Only the 5-phenyl isomer can give rise to this mass fragment. As there seems to be a mechanistic resemblance between the reaction of CSI with oxiranes and aziridines, the assignment of 5-phenyl isomeric structure to compounds **8-11** is more reasonable than the 4-phenyl isomeric structure.

The second component of the mixture, presumably the imidazolidone derivative **12**, could not be isolated from the mother liquor because of its instability. However, its presence in the reaction mixture was apparent by monitoring the carbonyl absorption (1745 cm^{-1}) by ir spectroscopy. The residue containing impure **12** when subjected to

hydrolytic work-up and subsequent chromatographic separation of the products led to the isolation of **16**. The ir spectrum of this compound showed broad absorption bands at 1650 (C=O) and 3200 (NH) cm^{-1}. For the imidazolidone carbonyl, the value of 1650 cm^{-1} appears to be lower than anticipated [6]. This was found to be due to the intermolecular hydrogen bonding, since the carbonyl absorption band showed a shift (1710 cm^{-1}), when the ir spectrum of **16** was run in carbon tetrachloride. The mass spectrum of **16** contained a peak with m/e 105 indicating the presence of a benzoyl substituent. From the foregoing discussion it is apparent that both the substituents, *viz.*, amide and benzoyl are present in **16** and the 1650 cm^{-1} band in ir spectrum is composite of two overlapping stretching frequencies, of these two carbonyl groups. The pmr and mass spectral data are in accordance with the assigned structure. The mass spectra of **16** and its analogues **17** and **18** showed three common prominent peaks at m/e 243, 161 and 118. The m/e 243 peak in all these cases is due to (M^+-aroyl) fragment, and the peaks at m/e 161 and 118 are the derivatives of this primary fragment m/e 243, *i.e.* (243-C_6H_{10}) and (161-CONH) [7]. The other possible regioisomeric structure for **16** was not favoured, for the same reasons given under **8**.

Compounds **5-7** were found to react with CSI in an analogous manner to yield the corresponding oxazolidine, **9-11** and imidazolidone, **17, 18**, derivatives.

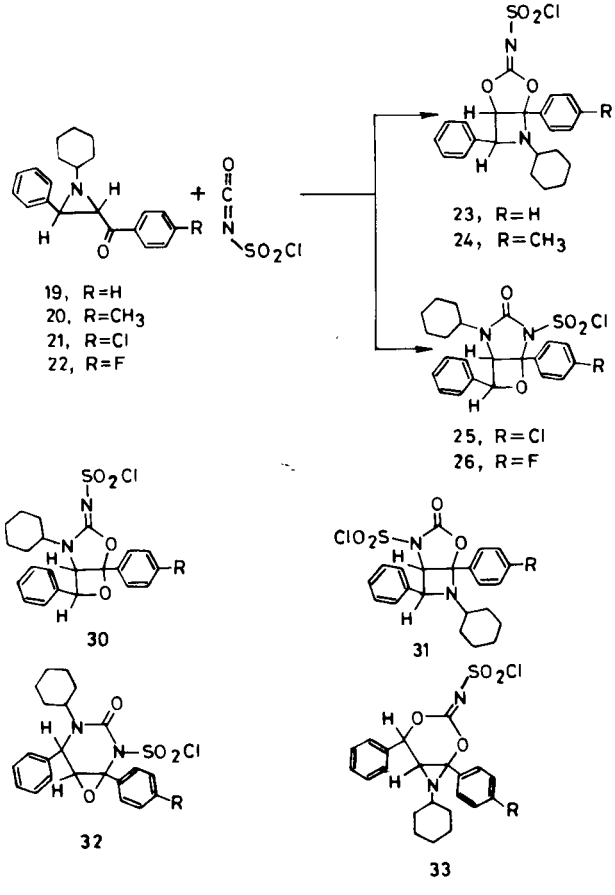
SCHEME 2



Based on the above observations a plausible mechanism can be advanced to explain the course of the reaction. The mechanism is analogous to the one proposed for the reaction of epoxides with CSI. Thus, the lone pair of electrons on nitrogen of the aziridine exerts a nucleophilic attack on the carbon of the isocyanate moiety, leading to the formation of the zwitterion **27**. The aziridinium ion thus produced, is highly unstable and is, therefore, susceptible to cleavage by the attack of the nucleophilic part of the zwitterion (Scheme 2). Since the reaction is stereospecific, it is logical to assume that the transformation of the zwitterion to the ring expanded product occurs in a near concerted fashion.

To confirm the stereospecific nature of these reactions, the corresponding *trans*-aziridines **19-22** were chosen as substrates. However, it is interesting to note that unusual products were formed in the reaction of **19-22** with CSI, by the participation of benzoyl carbonyl (Scheme 3).

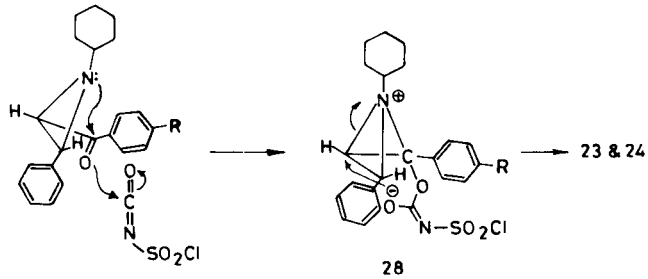
SCHEME 3



Thus, *trans*-1-cyclohexyl-2-benzoyl-3-phenylaziridine (**19**) reacted with CSI, at 0°, to produce **23** in 72% yield. Elemental analysis and mass spectral data showed it to be a 1:1 adduct. Its ir spectrum showed the absence of a benz-

oyl carbonyl. The presence of absorption bands located at 1580 (C=N), 1360, 1172 (SO_2) cm^{-1} indicate the presence of a chlorosulfonylimino function. The pmr spectrum exhibited two doublets at δ 4.84 (1H, J = 4.25 Hz) and δ 6.0 (1H, J = 4.25 Hz), due to the vicinal methine protons. The one proton multiplet at δ 4.25 can be attributed to the *N*-cyclohexyl methine proton. The presence of doublets, implies that the transformation involves only the C-N bond and the benzoyl carbonyl of the parent aziridine. Further, the base peak in the mass spectrum is at m/e 105, clearly points to the fact that in **23** the benzoyl oxygen forms a part of the ring system. Based on the above spectral data, **23** has been proposed the structure: 6-*N*-cyclohexyl-3-chlorosulfonylimino-1,7-diphenyl-2,4-dioxa-6-azabicyclo-[3.2.0]heptane. This is amply supported by the mass fragmentation pattern of the molecule. The toluoyl analogue **20** reacted with CSI in a similar manner, to yield **24**. Compound **24** exhibited similar spectral characteristics and was, therefore, assigned a similar structure.

SCHEME 4



The rationale for the formation of **23** and **24** is depicted in the Scheme 4. The carbonyl oxygen of the aziridine **19** and **20** initiates an attack on CSI, which in turn is assisted by the attack of nitrogen lone pair on carbonyl carbon, to give a bicyclic aziridinium ion intermediate **28**. This intermediate ion leads to the products **23** and **24** by the intramolecular attack of the oxyanion on the less hindered carbon. The structures **30** and **33** for the products were, however, ruled out based on the spectral data. This mechanism is analogous to the one reported for the reaction of thionyl chloride with aziridine [8].

Some interesting results have emerged when the above reaction was extended to the corresponding *p*-chloro- and *p*-fluorobenzoyl aziridines **21** and **22**. Thus **21** and **22** reacted with CSI to furnish products **25** and **26** respectively. The analytical and mass spectral data indicated that the products correspond to 1:1 adducts. The infrared analysis of **25** showed the conspicuous absence of the benzoyl carbonyl. However, the presence of absorption bands, namely, 1740, 1390, 1160 cm^{-1} can be ascribed to be due to imidazolidone and sulfonyl substituents. The pmr spectrum of **25** exhibited a doublet due to aromatic protons at δ7.36, a multiplet centered at δ 1.6 due to methylene protons, and a pair of doublets at δ 5.5 and δ 4.1 with a coupling constant J = 4.5 Hz. These pair of doublets can be attributed to the vicinal methine protons. Further, the one proton multiplet at 3.8 is assigned to the *N*-cyclohexyl methine proton. The mass spectrum of **25** contains a peak at m/e 381 (M^+-SO_2Cl), indicating the presence of a chlorosulfonyl group. Besides, the mass spectrum exhibited a mass peak at m/e 374 (M^+-106) and two prominent peaks at m/e 105 and 106 respectively. These peaks were also found in the mass spectrum of **26**. This suggests the presence of a C_6H_5CH-O- residue in these molecules. In light of these evidences the adducts have been assigned the structures **25** and **26** respectively. Other alternative structures such as **31** and **32** are ruled out as these do not satisfactorily explain the spectral data. The formation of **25** and **26** can be visualized as shown in Scheme 4.

From the foregoing discussions it is apparent that two different types of mechanisms are involved in the formation of **23** and **24**, and **25** and **26** respectively. The difference arises presumably due to the difference in the electronic effects of the substituents (*viz.* H, CH_3, Cl, F) present in the aroyl moiety of the aziridine molecule. The difference in the type of products obtained when *cis*- and *trans*-aziridines are reacted with CSI, can be explained in terms of the involvement of steric factors.

In conclusion it may be pointed out here that the reaction of aziridines with CSI is of versatile nature. it is evident from the present study that an extensive investigation in this area would lead to the synthesis of several novel heterocyclic systems.

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fisher-Johns melting point apparatus. The ir spectra were recorded on a Perkin Model-580, or Model-377, infrared spectrophotometers. The pmr spectra were recorded on a Brucker-WP 80 (80 MHz) or Varian EM-390 (90 MHz) spectrometers. Chemical shifts are reported in parts per million downfield from internal reference TMS (δ). Multiplicity is indicated using the following abbreviations: s (singlet), bs (broad singlet), d (doublet), t (triplet) and q (quartet). Mass spectra were recorded on a Jeol JMS-300D mass spectrometer at 70 eV. The elemental anasyses were carried out in Coleman automatic carbon, hydrogen and nitrogen analysers. CSI (Fluka), ether (dried over sodium) and dichloromethane (distilled from phosphorus pentoxide) were used in the experiments. Aziridines **1** [9] **4-7**

and **19-22** [10] were prepared by known procedures.

cis-2-Chlorosulfonylimino-3,4,5-triphenyl-1,3-oxazolidine (**2**).

A solution of CSI (0.18 ml, 0.002 mole) in ether-dichloromethane (4:1, 10 ml) was added dropwise, with stirring, to a solution of **1** (0.540 g, 0.002 mole) in the same solvent system (15 ml), over a period of five minutes at 0°. The reaction mixture was stirred for thirty minutes and poured into water (10 ml). The organic layer was separated, washed with water, dried over sodium sulfate and the solvent was evaporated off to obtain a solid residue. It was crystallized from chloroform-petroleum ether to obtain **2** in colorless needles. See Table 1 and Table 2 for physical, analytical and spectral data of **2**.

3,4,5-Triphenyl-1,3-oxazolidin-2-one (**3**).

Compound **2** (0.205 g, 0.0005 mole) was dissolved in an acetone-water mixture (9:1, 20 ml) and the resulting acidic solution was neutralized by slow addition of 5% aqueous potassium hydroxide. This mixture was stirred for thirty minutes and diluted with water. A solid separated out, which was extracted with dichloromethane (3 × 20 ml). The organic layer was washed with water and dried over anhydrous sodium sulfate, and the solvent evaporated off. The solid residue on crystallization from ethanol furnished the title compound **3**, yield 0.130 g (82%), mp 215-216°, lit [5] mp 216°; ir (potassium bromide): 1730 (C=O) cm^{-1}; ms: (m/e) 315 (molecular ion) 271 (M^+-CO_2).

Reaction of CSI with **4**. Preparation of *cis*-2-Chlorosulfonylimino-3-cyclohexyl-4-benzoyl-5-phenyl-1,3-oxazolidine (**8**) and *cis*-3-Cyclohexyl-4-benzoyl-5-phenyl-1,3-imidazolidin-2-one (**16**).

To a magnetically stirred solution of **4** (0.305 g, 0.001 mole) in ether (20 ml) was added dropwise a solution of CSI (0.09 ml, 0.001 mole) in ether (5 ml) at 0°. A white pecipitate was formed within five minutes. Stirring was continued for a further fifteen minutes and the solid filtered off. The filtrate (A) obtained was reserved for hydrolytic workup. The solid obtained was crystallized from chloroform-petroleum ether (20:1), to get 0.3 g of pure **8**. The solvent was evaporated off from the filtrate **A** and the solid residue thus obtained was taken up in aqueous acetone (9:1, 20 ml). The resulting acidic solution was neutralized at room temperature by adding dropwise 5% aqueous potassium hydroxide solution and allowed to stand for thirty minutes. The aqueous mixture was extracted with dichloromethane (3 × 20 ml). The combined dichloromethane extracts were washed with water and dried over anhydrous sodium sulfate. The oily liquid, obtained after the removal of the solvent, was flash chromatographed (silica gel (tlc) eluant: ether-petroleum ether (1:4) and ether-ethyl acetate (4:1)). The ether-ethyl acetate eluted fractions furnished **16** which was purified by crystallization from dichloromethane-petroleum ether (10:1), yield 0.065 g (19%), mp 188-189°.

The compounds **9-11, 17** and **18** were prepared in an analogous manner. The yield, mp, analytical and spectral data are collected in Table 1 and Table 2.

6-*N*-Cyclohexyl-3-chlorosulfonylimino-1,7-diphenyl-2,4-dioxa-6-azabicyclo[3.2.0]heptane (**23**).

To a magnetically stirred solution of **19** (0.305 g, 0.001 mole) in dry ether (20 ml) was added dropwise CSI (0.09 ml, 0.001 mole) in dry ether (10 ml) at 0°. The mixture was stirred for ten minutes and the solvent evaporated off to furnish an oil. The oil was dissolved in minimum quantity of dichloromethane and petroleum ether was added, dropwise to the solution till incipient turbidity. It was set aside for fifteen minutes for the crystallization to begin. Compound **23** separated in the form of colorless crystals, yield 0.320 g (72%), mp 124-125°; ir (potassium bromide): 2940, 2840 (CH_2), 1580 (C=N), 1360, 1172 (SO_2) cm^{-1}; pmr (deuteriochloroform): δ 7.69 (d, 10H aromatic), 6.0 (d, 1H, J = 4.25 Hz, C-1H), 4.84 (d, 1H, J = 4.25 Hz, C-7H), 4.1-4.3 (m, 1H, *N*-cyclohexyl methine proton), 1.0-2.1 (m, 10H, cyclohexyl CH_2-); ms: m/e 446 (M^+, 0.4), 411 (M^+-Cl, 0.2), 410 (M^+-HCl, 0.8), 364 (1.3), 346 (8), 340 (12), 327 (5), 304 (3), 258 (16), 242 (10), 187 (6), 161 (15), 118 (8), 105 (100), 104 (30), 91 (8), 83 (35), 77 (45), 64 (45).

Anal. Calcd. for $C_{22}H_{23}ClN_2O_4S$: C, 59.14; H, 5.15; N, 6.27. Found: C, 59.23; H, 5.30; N, 6.38.

6-*N*-Cyclohexyl-3-chlorosulfonylimino-5-tolyl-7-phenyl-2,4-dioxa-6-azabicyclo[3.2.0]heptane (**24**).

CSI (0.09 ml, 0.001 mole) in ether (5 ml) was added dropwise to a magnetically stirred solution of **20** (0.320 g, 0.001 mole) in dry ether (20 ml) at 0°. After fifteen minutes the solvent was evaporated off. A pasty mass was obtained which was flash chromatographed over silica gel (tlc) using ether-petroleum ether (1:4) as the eluant. The pure compound **24** obtained weighed 0.320 g (70%), mp 137-138°; ir (potassium bromide): 2924, 2840 (CH_2), 1575 (C=N), 1350, 1178 (SO_2) cm^{-1}; pmr (deuteriochloroform): δ 7.66 (d, 9H, aromatic), 6.0 (d, 1H, J = 4.25 Hz, C-1H), 4.81 (d, 1H, J = 4.25 Hz, C-7H), 4-4.45 (m, 1H, *N*-cyclohexyl C-H), 2.52 (s, 3H, CH_3), 1.0-2.15 (m, 10H, cyclohexyl CH_2-); ms: m/e 460 (M^+, 0.3), 459 (M^+-1, 0.4), 424 (1.4), 378 (1.6), 361 (3.4), 360 (3.4), 352 (3.5), 341 (8.3), 289 (3), 258 (10), 243 (10), 180 (3), 161 (10), 119 (100), 91 (40), 83 (20), 77 (20), 64 (30).

Anal. Calcd. for $C_{23}H_{25}ClN_2O_4S$: C, 59.94; H, 5.43; N, 6.08. Found: C, 59.82; H, 5.32; N, 6.21.

4-*N*-Chlorosulfonyl-2-*N*-cyclohexyl-3-oxo-5-(4′-chlorophenyl)-7-phenyl-6-oxa-2,4-diazabicycloz[3.2.0]heptane (**25**).

To a stirred solution of **21** (0.340 g, 0.001 mole) in dry ether (15 ml) was added CSI (0.09 ml, 0.001 mole) at 0°. Evaporation of the solvent after fifteen minutes left a residue, which was flash chromatographed (silica gel, tlc grade) using ether-petroleum ether (1:4) as eluant. Compound **25** was obtained as colorless crystals, yield 0.330 g (69%) mp 164-165°; ir (potassium bromide): 2905, 2830 (CH_2), 1740 (CO), 1390, 1160 (SO_2) cm^{-1}; pmr (deuteriochloroform): δ 7.36 (d, 9H, aromatic), 5.5 (d, 1H, J = 4.5 Hz, C-1H), 4.1 (d, 1H, J = 4.5 Hz, C-7H), 3.7-3.9 (m, 1H, *N*-cyclohexyl C-H), 0.9-1.8 (m, 10H, cyclohexyl CH_2); ms: m/e 480 (M^+, 0.4), 381 (M^+-SO_2Cl, 0.3), 375 (1.4), 374 (4), 312 (8.3), 310 (12.6), 273 (70), 230 (50), 228 (65), 194 (40), 193 (60), 166 (15), 158 (20), 139 (40), 138 (38), 111 (15), 106 (70), 105 (82), 83 (25), 77 (100), 64 (55).

Anal. Calcd. for $C_{22}H_{22}ClN_2O_4S$: C, 54.91; H, 4.57; N, 5.82. Found: C, 54.82; H, 4.64; N, 5.73.

2-*N*-Cyclohexyl-4-*N*-chlorosulfonyl-3-oxo-5-(4′-fluorophenyl)-7-phenyl-6-oxa-2,4-diazabicyclo[3.2.0]heptane (**26**).

The compound **26** was prepared in a similar manner as desribed above, using **22** (0.325 g, 0.001 mole) and CSI (0.09 ml, 0.001 mole), yield 0.330 g (71%), mp 159-160°; ir (potassium bromide): 2915, 2835 (CH_2), 1740 (C=O), 1390, 1170 (SO_2) cm^{-1}; pmr (deuteriochloroform): δ 7.1-7.7 (m, 9H, aromatic), 5.68 (d, 1H, J = 4.5 Hz, C-1H), 4.33 (d, 1H, J = 4.5 Hz, C-7H), 3.9-4.1 (m, 1H, *N*-cyclohexyl C-H), 0.9-2.1 (m, 10H, $(CH_2)_5$); ms: m/e 464 (M^+, 0.3), 365 (M^+-SO_2Cl, 0.4), 358 (2), 294 (10), 274 (2), 260 (26), 259 (47), 212 (60), 178 (80), 177 (40), 150 (10), 123 (25), 122 (60), 106 (82), 105 (80), 95 (20), 83 (15), 77 (100), 64 (75), 55 (50).

Anal. Calcd. for $C_{22}H_{22}FClN_2O_4S$: C, 56.85; H, 4.74; N, 6.03. Found: C, 56.96; H, 4.85; N, 6.21.

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