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CYCLOADDITION OF CHLOROSULFONYL ISOCYANATE TO 2H-AZIRINES: FORMATION OF [2+2+2] CYCLOADDUCTS

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Abstract - Chlorosulfonyl isocyanate (CSI) reacts with 2H-azirines **1a-c** at -78°C to form [2+2+2] cycloadducts **3a-c** and **4a-c**. The tricyclic aziridine derivatives **4a-c** undergo CSI extrusion reactions and subsequent oxidation to the corresponding pyrazines **5a-c**. Structural identifications of **3a-c** and **4a-c** are based on ir, nmr and mass spectral data.

Dipolar cycloaddition reactions of small ring heterocycles with the highly reactive heterocumulene chlorosulfonyl isocyanate (CSI, $O=C=N-SO_2-Cl$) involve both C=O and C=N of the isocyanate under mild experimental conditions[1a-b]. The ratio of C=O and C=N addition products is found to vary with temperature, catalyst and nature of the substrate[1b,2].

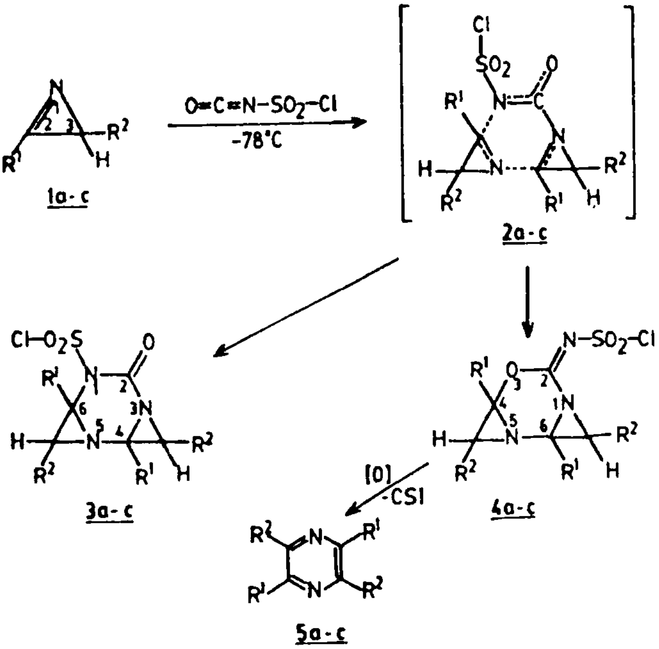
2H-Azirines are known to be relatively unreactive towards simple isocyanates[3]. However, benzoyl, thiobenzoyl, and p-tolylsulfonyl isocyanates are found to undergo thermal symmetry allowed $[\pi^4s+\pi^2s]$, $[\pi^2s+\pi^2a]$ and $[\pi^2s+\pi^2s+\pi^2s]$ pericyclic reactions[3-5] with 2H-azirines. The reactive π bond of 2H-azirine participates as a component in all these cycloaddition reactions. We wish to report the formation of tricyclic aziridine derivatives **3a-c**, **4a-c** by the cycloaddition reaction of CSI with 2H-azirine at -78°C.

RESULTS AND DISCUSSION

A solution of 3-phenyl-2H-azirine **1a** on treatment with CSI for thirty minutes at -78°C gave, a white crystalline compound **5a** (20 mg, 8.5% yield based on 2H-azirine), mp 195°C, a pale yellow compound **3a**, (125 mg, 53.4%) mp 95°C, and a dark brown solid **4a** (80 mg, 34.2%) mp 105°C. The physical and spectral data of **5a** are in good agreement with those reported[6] for 2,5-diphenylpyrazine.

The conclusion that **3a** and **4a** are made up of one CSI and two aziridine moieties is based on the molecular ion (m/e 375) and the mass fragmentation pattern of these compounds. Thus the appearance of prominent mass fragment ions, viz., m/e 43(CONH), 103(C_6H_5CN), 262(M^+-NSO_2Cl), 276(M^+-SO_2Cl), 347(M^+-CO) for **3a** shows that it is a C=N adduct of CSI with **1a**. While on the other hand the prominent ions in **4a** corresponding to m/e 44 (CO_2), 105 (C_6H_5CO), 234 (M^+-CSI), 278 (M^+-NSOCl) indicate that it is a C=O adduct of CSI with **1a**.

The presence of aziridine moieties in compounds **3a** and **4a** was confirmed by ^{1}H-nmr and ^{13}C-nmr spectral data. Thus in both compounds the four aziridine protons show up as multiplets located at δ 3.1-3.7 and 4.7-5.7 respectively. The presence of an oxygen atom in the ring structure of **4a** is responsible for the downward chemical shift of its aziridine protons by 1.6-2 ppm. The ^{13}C-nmr spectrum of **3a** showed the carbonyl and aziridine carbons at δ 171.01 (C_2) and 52.53 (d, aziridine carbons). The imino and aziridine carbons of **4a** appeared at δ 157.85



1a - 5a R^1 = C$_6$H$_5$, R^2 = H
1b - 5b R^1 = p-Me-C$_6$H$_4$, R^2 = H
1c - 5c R^1 = p-Cl-C$_6$H$_4$, R^2 = H

SCHEME

(C$_2$) and 61.21 (d, aziridine carbons). The ring carbons of **3a** appeared as doublets at δ 121.89 (C$_4$, C$_6$), while in the case of **4a** there were two separate peaks viz., at δ 143.77 (C$_4$) and 111.07 (C$_6$) respectively. The ir absorption bands (1690 (C=0), 1390, 1190, 1060 (SO$_2$-Cl) cm^{-1}) of **3a** confirmed the presence of C=O and SO$_2$-Cl moieties within the molecule. Similarly the presence of C=N and SO$_2$-Cl moieties in **4a** was confirmed by its ir (1610 (C=N), 1380, 1160 (SO$_2$-Cl), 1080 (cm^{-1}) spectrum.

The position of the phenyl rings in **3a** and **4a** was confirmed by the comparison of their prominent mass fragmentation ions corresponding to m/e 103 (C_6H_5CN), 105 (C_6H_5CO) respectively. An additional support to the above view was provided by the isolation of 2,5-diphenylpyrazine, **5a**, which is the extrusion product of **4a**. Compound **4a**, in contact with atmospheric moisture, is converted to **5a**, within a few days. The compound **3a** on the other hand, is relatively more stable than **4a**, but subsequently gets converted into a ring enlarged product[7].

Compounds **1b-c** were found to react with CSI in an analogous manner as described earlier to yield the tricyclic aziridine derivatives **3b-c**, **4b-c** and pyrazines **5b-c** respectively. Compound **4b** was found to be highly unstable, and gets converted into **5b** during the work-up operation.

The rationale for the formation of **3**,**4** and **5** is depicted in the Scheme. Thus CSI adds across the two reactive bonds of two 2H-azirine molecules in two alternate modes. One mode of addition (C=N addition of CSI) produced the tricyclic aziridine derivative **3**. Second mode of addition (C=O) resulted in the formation of **4**. The pyrazine **5** was formed by the extrusion of CSI from **4** and subsequent oxidation during work-up operation.

EXPERIMENTAL

Reaction of CSI with 3-phenyl-2H-azirine: General procedure (3a-c; 4a-c; 5a-c)

A solution of CSI (0.002 mol, 0.18 ml) in dry dichloromethane (5 ml) was added dropwise to a solution of **1a**[8] (0.002 mol, 0.234 g) in the same solvent (20 ml)

TABLE -Reaction of CSI with 2H-azirines **1a-c**

Product	Yield %	mp °C	Mass m/e (%)
3a	53.4	95	375 (M^+), 43 (100)
3b	55.3	150	403 (M^+), 43 (100)
3c	53.2	178	423 (M^+), 43 (100)
4a	34.2	105	375 (M^+), 44 (100)
4b	26.8	140	403 (M^+), 80 (100)
4c	26.6	192	423 (M^+), 44 (100)
5a	8.6	195	232 (M^+), 77 (100)
5b	11.5	180	260 (M^+), 91 (100)
5c	8.3	171	300 (M^+), 43 (100)

at -78°C for a period of ten minutes. The reaction mixture was stirred for thirty minutes at the same temperature and the solvent was removed under diminished pressure. The residue was flash chromatographed using silica-gel. The products were eluted with petroleum ether-ether and ether-acetone.

Petroleum ether-ether (4:1) eluted fraction furnished 20 mg (8.60%) of **5a** as white needles; mp 195°C (lit[6]; mp 195-196°C); ^{1}H-nmr (80 MHz, $CDCl_3$, TMS); δ 7.15 (s, 1H), 7.5 (t, 6H), 8.0 (q, 4H), 8.95 (s, 1H); ms: m/e 232 (M^+), 77 (100).

Ether-acetone (1:1) eluted fraction gave dark brown crystals of **4a** (80 mg, 34.20%); mp 105°C; ir (KBr): 1610, 1600, 1460, 1380, 1240, 1160, 1080, 860, 760, 710 cm^{-1} ; ^{1}H-nmr (400 MHz, $(CD_3)_2SO$, TMS): δ 4.7- 5.7 (m, 4H), 7.0-8.2 (m, 10H); ^{13}C-nmr (100 MHz, $(CD_3)_2SO$, TMS); δ 157.85, 143.77, 134.30, 130.25, 129.14, 129.04, 128.23, 126.67, 125.60, 125.33, 124.99, 123.27, 111.07, 61.21; ms: m/e 375 (M$^+$), 357, 292, 278, 234, 232, 175, 159, 105, 104, 101, 76, 64, 44, 42.

Further elution with ether-acetone (1:2) furnished light yellow crystals of **3a** (125 mg, 53.4%); mp 95°C; ir (KBr): 1690 , 1600, 1490, 1450, 1390, 1310, 1230, 1190, 1060, 890, 850, 760, 700, 600 cm^{-1}; ^{1}H-nmr (400 MHz, $(CD_3)_2SO$, TMS): δ 3.1-3.7 (m, 4H), 7.0-8.0 (m, 10H); ^{13}C-nmr (100 MHz, $(CD_3)_2SO$, TMS): δ 171.01, 131.18, 130.77, 129.58, 129.24, 128.60, 128.29 123.84, 123.54, 121.89, 52.53 ; ms, m/e: 375 (M$^+$), 347, 279, 278, 276, 274, 262, 261, 260, 247, 246, 234, 232, 231, 220, 203, 189, 173, 159, 104, 102, 76, 64, 43.

Compounds **3b-c, 4b-c** and **5b-c** were characterized by ir, nmr (^{1}H, ^{13}C) and mass spectral studies. The yields, melting points and the mass data of these compounds are collected in Table.

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