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Cycloaddition of Chlorosulfonyl Isocyanate with Arylmethylenemalonaldehydes

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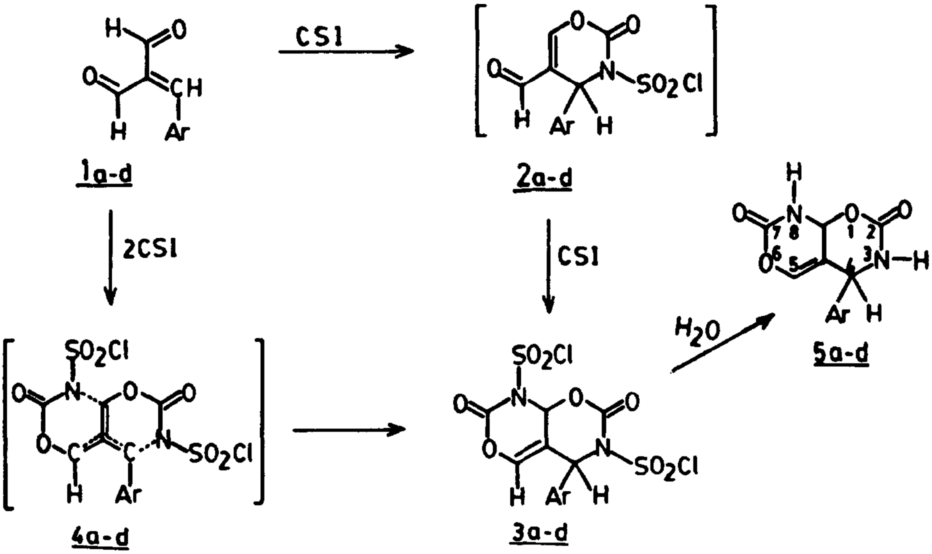
Abstract - The reaction of chlorosulfonyl isocyanate with arylmethylenemalonaldehydes afforded the fused 1,3-oxazin-2-one derivatives.

Aldehydes are reported to react with chlorosulfonyl isocyanate ($O=C=N-SO_2Cl$, CSI) to give six membered heterocycles as well as acyclic chlorosulfonylimino derivatives. However, the reaction of CSI with ketones gives different products depending upon the structure of the ketones.[1] Vinyl ketones are reported to give [4+2] as well as [2+2] cycloadducts with CSI. Arylmethylenemalonaldehydes[2] are reported to play the role of 4π and 2π components in many cycloaddition reactions to form the new family of heterocyclic carboxaldehydes.[3] The 2π component used in these reactions vary from simple olefins to highly activated ketene acetals. However, there is no literature report regarding the reactivity of these 1,1-dialdehydes towards the most reactive heterocumulene, CSI. We have carried out the reaction of 1,1-dialdehydes (1a-e) with CSI and obtained the oxazinone derivatives (5a-d and 7e).

Arylmethylenemalonaldehyde (1a) and CSI reacted smoothly at 0-5°C to give 5a in fairly good yield (67%). The product showed the mass molecular ion at m/e: 280 and prominent fragment ions at m/e: 237 (M^+ - CONH), 236 ($M^+ - CO_2$), 221 ($M^+ - CO_2NH$), 192 ($M^+ - 2CO_2$), 179 (M^+ - CHOCONHCHO), 164 ($M^+ - NH_2CO_2CHNHCHO$), 137 (ClC_6H_4CN), 130 ($-C_6H_4CHCCHO-$) and 44 (CO_2), which indicate the presence of two -CONH- groups in the molecule. This conclusion was supported by the ir spectrum [3400, 1720, 1650, 1590 (CO_2NH) cm^{-1}] of the molecule. The ^1H-nmr of 5a contained two singlets at δ 2.40 and 3.05 (Ar-CH- , -CH-O-) and two broad deuterium exchangeable signals at δ 5.50 and 5.80-6.20 (-NH-) in the ratio 1:1:1:1. The singlet at δ 7.85 is assigned to the olefinic proton. The microanalytical data of the product is consistent with the molecular formula, $C_{12}H_9ClN_2O_4$. Based on these spectral and analytical data the product was assigned the structure 5a (Scheme 1).

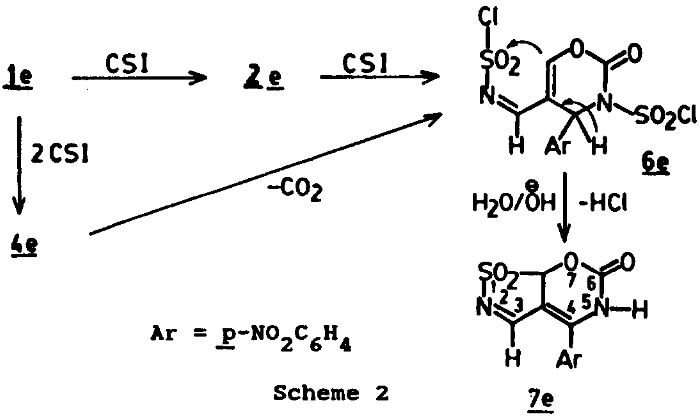
The dialdehydes 1b-d reacted with CSI in an identical manner and gave the corresponding oxazinone derivatives (5b-d). 4-Nitrophenylmethylenemalonaldehyde (1e) on reaction with CSI under similar experimental conditions gave a new oxazinone derivative (7e) (Scheme 2). The product was characterized as follows: It showed the molecular ion at m/e: 309 and prominent fragment ions at m/e: 150 ($NO_2C_6H_4CHNH$), 148 ($NO_2C_6H_4CN$), 64 (SO_2) and 43 (CONH) in its mass spectrum, which indicate the presence of $-SO_2-$ and -CONH- moieties in the molecule. The ir spectrum [3350, 1660, 1600 (-CONH-), 1340, 1180 ($-SO_2-$) cm^{-1}] of the product is in good agreement with the above conclusion. The ^1H-nmr spectrum of 7e showed two sharp singlets at δ 3.25 (SO_2-CH-O), 6.85 (-N=CH-) and a broad deuterium exchangeable peak at δ 5.95 (-NH-) in the ratio 1:1:1, which are consistent with the assigned structure, 7e.

The formation of 5a-d can be pictured as shown in scheme 1. Thus, CSI cycloadds to the 1,1-dialdehydes (1a-d) in a [4+2] manner to form the N-chlorosulfonyloxazinones (2a-d). These cycloadducts (2a-d) undergo further [4+2] cycloaddition reaction with CSI to form 5a-d through the intermediacy of 3a-d. Alternatively the cycloaddition may occur in a single step through the intermediacy of 4a-d. This type of "criss-cross" addition was reported in the case of CSI and aldazines.[4]



a-d: Ar = p-ClC_6H_4, p-BrC_6H_4, o-ClC_6H_4, p-MeC_6H_4
Scheme 1

The formation of 7e can be visualized as shown in scheme 2. The initially formed cycloadduct (2e) of 1e and CSI undergoes further reaction with CSI in a [2+2] manner to form 6e. The participation of aldehydes as 2π component in the cycloaddition reaction with CSI has been reported in literature.[1] Here the presence of electron withdrawing (NO_2) group at the para position of the phenyl ring of 1e may be favoring the [2+2] cycloaddition path rather than [4+2]. Finally the intermediate 6e undergoes cyclocondensation to 7e during aqueous work-up. The electron withdrawing $-NO_2$ group makes the hydrogen atom adjacent to the phenyl ring acidic, so that elimination of HCl from 6e to form 7e is favored. Alternatively 6e can also be formed via the intermediate 4e (Scheme 2).



Scheme 2

EXPERIMENTAL

All melting points were determined on a Fisher - Johns melting point apparatus and are uncorrected. The ir spectra were taken on Perkin - Elmer FT ir (1600) spectrophotometer. Mass spectra were recorded on a Jeol - JMS - 300D mass spectrometer. Chemical shifts are reported in parts per million down field from internal reference TMS (δ). Multiplicity is indicated by the following abbreviations: s (singlet), b (broad), and m (multiplet). The elemental analyses were carried out in a Colman automatic carbon, hydrogen and nitrogen analyzer. CSI was purchased from Fluka, AG, Switzerland and was used as such. Aldehydes 1a-e were prepared according to the reference 2.

Reaction of CSI with 1a-e: Preparation of 5a-d and 7e (General method). - To a stirred solution of the dialdehyde 1 (0.002 mol) in dry dichloromethane-benzene (20 ml, 1:1) at 0-5°C was added CSI (0.36 ml, 0.004 mol) in dry benzene (5 ml). The reaction mixture was stirred for 30 min. at room temperature (≈ 25°C) and the solvent was removed under reduced pressure. The residue was taken in acetone-water (20 ml, 9:1) and was neutralized with KOH solution (5%). The aqueous mixture thus obtained was extracted with dichloromethane and the combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Compounds 5 and 7 were recrystallized from dichloromethane-ether (1:1) and dichloromethane-petroleum ether (1:1) respectively.

5a: mp. 220°C; yield: 67%; ir (KBr), ν_{max}: 3400, 1720, 1650, 1590, 1500, 1230, 1030, 810, 760 cm^{-1}; ms, m/e (rel. int.): 282 (M^++2), 280 (M^+, 2), 249 (10), 247 (27), 239 (4), 238 (5), 237 (12), 236 (10), 223 (18), 221

(55), 212 (65), 203 (12), 194 (15), 192 (40), 181 (8), 179 (28), 166 (40), 165 (45), 164 (23), 158 (70), 155 (4), 153 (15), 139 (35), 137 (78), 130 (100), 102 (75), 76 (70), 44 (75); ^{1}H-nmr (CDCl$_3$), δ: 2.40 (s, 1H), 3.05 (s, 1H), 5.50 (b, 1H, NH), 5.80-6.20 (b, 1H, NH), 7.50 (m, 4H), 7.85 (s, 1H); Anal. Calcd for $C_{12}H_9ClN_2O_4$: C, 51.35; H, 3.23; N, 9.98; Found: C, 50.89 H, 3.02; N, 9.62.

5b: mp. 95°C; yield: 73%; ir (KBr), ν_{max}: 3428, 1710, 1630, 1587, 1485, 1406, 1183, 832 cm^{-1}; ms, m/e (rel. int.): 324 (M$^+$, 4), 298 (6), 296 (7), 288 (13), 286 (15), 283,(8), 282 (12), 281 (10), 280 (15), 238 (6), 236 (7), 225 (40), 223 (48), 210 (25), 208 (27), 205 (24), 201 (35), 199 (35), 184 (95), 183 (67), 182 (100), 181 (67), 156 (32), 154 (32), 76 (17), 49 (27), 44 (32); ^{1}H-nmr (CDCl$_3$), δ: 1.95 (s, 1H), 3.00 (s, 1H), 3.75 (b, 1H, NH), 3.95 (b, 1H, NH), 7.40-7.50 (m, 4H), 7.75 (s, 1H); Anal. Calcd for $C_{12}H_9BrN_2O_4$: C, 44.33; H, 2.79; N, 8.61; Found: C, 43.71; H, 2.48; N, 8.71.

5c: mp. 160°C; yield: 74%; ir (KBr), ν_{max}: 3300, 1720, 1640, 1600, 1040, 830 cm^{-1}; ms, m/e (rel. int.): 282 (M$^+$+2, 2), 280 (M$^+$, 7), 238 (8), 236 (27), 223 (5), 221 (20), 212 (6), 209 (17), 200 (25), 194 (10), 192 (32), 181 (8), 179 (30), 166 (12), 164 (25), 139 (24), 137 (70), 125 (70), 116 (32), 114 (85), 76 (40), 44 (100); ^{1}H-nmr (CDCl$_3$), δ: 2.35 (s, 1H), 3.05 (s, 1H), 5.60-6.00 (b, 2H, NH), 7.50 (m, 4H), 7.80 (s, 1H); Anal. Calcd for $C_{12}H_9ClNO_4$: C, 51.35; H, 3.23; N, 9.98; Found: C, 50.97; H, 3.11; N, 9.64.

5d: mp. 136°C; yield: 88%; ir (KBr), ν_{max}: 3340, 3000, 2920, 1740, 1660, 1590, 1500, 1240, 1040, 800, 750 cm^{-1}; ms, m/e (rel. int.): 260 (M$^+$, 2), 216 (25), 201 (20), 172 (40), 157 (15), 119 (48), 117 (62), 104 (80), 91 (100), 88 (70), 76 (40), 44 (85); ^{1}H-nmr (CDCl$_3$), δ: 2.40 (s, 4H), 3.05 (s, 1H), 6.00 (b, 2H, NH), 7.50 (m, 4H), 7.85 (s, 1H); Anal. Calcd for $C_{13}H_{12}N_2O_4$: C, 59.99; H, 4.64; N, 10.76; Found: C, 59.53; H, 4.46; N, 10.52.

7e: mp. 118°C; yield: 64%; ir (KBr), ν_{max}: 3350, 1690, 1660, 1600, 1510, 1340, 1180, 1110, 1050, 850, 750, 700 cm^{-1}; ms, m/e (rel. int.): 309 (M$^+$, 2), 225 (12), 190 (25), 175 (30), 150 (55), 148 (50), 103 (35), 76 (70), 64 (100), 44 (48), 43 (20); ^{1}H-nmr (CDCl$_3$), δ: 3.25 (s, 1H), 5.95 (b, 1H, NH), 6.85 (s, 1H), 7.40-7.80 (m, 4H); Anal. Calcd for $C_{11}H_7N_3O_6S$: C, 42.72; H, 2.28; N, 13.58; Found: C, 42.51; H, 2.09; N, 13.46.

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