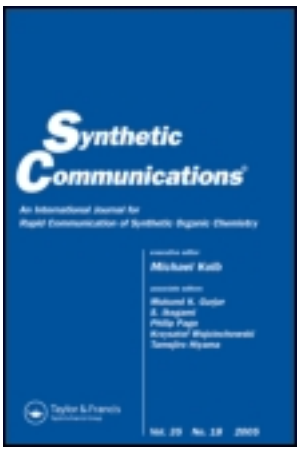

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A Facile Synthesis of Triazocinones and Oxadiazocinones

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A FACILE SYNTHESIS OF TRIAZOCINONES AND OXADIAZOCINONES

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Abstract - A facile synthesis of 4,7-diaryl-1,3,6-trihydro-1,3,6-triazocin-2-ones and 5,8-diaryl-3,6-dihydro-1,3,6-oxadiazocin-2-ones is reported by the interaction of chlorosulfonyl isocyanate and 2H-azirines.

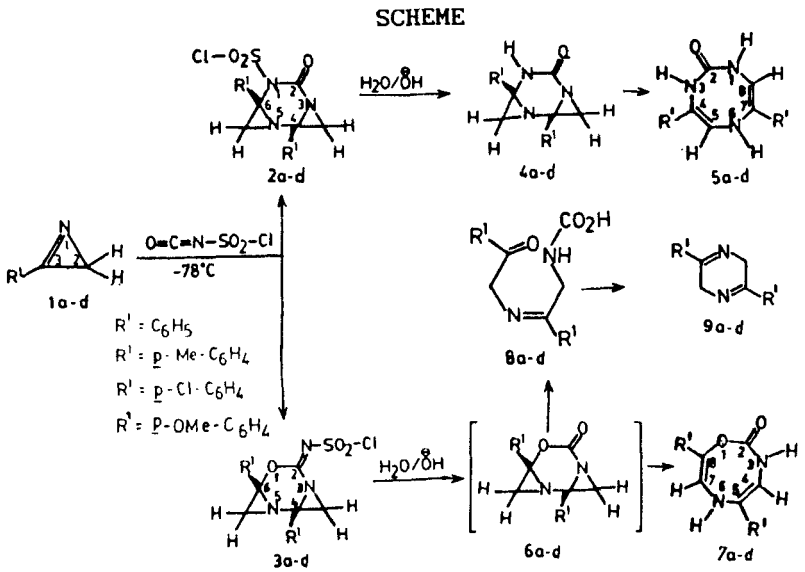
In contrast with other isocyanates chlorosulfonyl isocyanate (CSI, O=C=N-SO_2Cl) is reported[1] to react with oxiranes and their nitrogen analogues across the C=N and C=O groups. Recently we have reported[2] a thermal symmetry allowed [π^2s+π^2s+π^2s] cycloaddition reaction of CSI with 2H-azirines to form the [2+2+2] cycloadducts and the rearranged products (pyrazines). Both C=N and C=O groups of CSI participate as a 2π component in these cycloaddition reactions. Hydrolysis of the [2+2+2] cycloadducts resulted in the formation of the ring enlarged heterocycles, the azocine derivatives.

Thus the C=N adduct (**2a**) [of CSI and 3-phenyl-2H-azirine (**1a**)] was converted into the corresponding ring enlarged product, the triazocine derivative (**5a**), by hydrolysis. However, the C=O adduct (**3a**), under similar experimental conditions, gave the corresponding ring enlarged product, the oxadiazocinone derivative (**7a**) and the rearranged product, 2,5-diphenylpyrazine (**9a**[2]), in the ratio 45:54 (scheme). Alternatively **5a**, **7a**, and **9a** were obtained (in the ratio 47:25:10) by the reaction of **1a** and CSI at -78 °C, and subsequent hydrolysis (without isolating **2a** and **3a**).

The physical and spectral data of **9a** are in good agreement with the structure: 2,5-diphenylpyrazine.[2] Its formation from the C=O adduct (**3a**) can be visualized in terms of an extrusion of CO_2 from **8a**, through the intermediacy of **6a** followed by cyclocondenzation and oxidation during hydrolytic work-up. Alternatively **9a** can be formed by the extrusion of CSI from **3a**, followed by rearrangement and oxidation. Ring enlargement of **4a** and **6a** leads to the formation of **5a** and **7a** respectively.

Azocine derivatives **5a** and **7a** were identified as follows: The ^{1}H-nmr spectrum of **5a** contained deuterium exchangeable proton signals at δ 3.05 and 10.15 (in the ratio 2:1) arising from three -NH- moieties. The conspicuous

SCHEME



absence of an aziridine proton signal and the presence of two olefinic protons signals at δ 5.15 (s) and 6.30 (s) in the ratio 1:1 indicate that **5a** is formed by the cleavage of N_3-C_4 and N_5-C_6 bonds of **4a** followed by rearrangement. This conclusion was further substantiated by the ^{13}C-nmr [δ 193.00 (C_2), 155.01, 133.13 (C_4, C_5, C_7, C_8)] spectral data of the compound. The ir absorption band at 1690 cm^{-1} is characteristic for -NH-CO-NH- moiety. The conclusion that **7a** is formed by the ring enlargement (N_3-C_4 and N_5-C_6 bonds cleavage) of **6a** was confirmed by the nmr (^{1}H and ^{13}C) spectral characteristics of **7a**. The ^{1}H-nmr spectrum of **7a** showed a deuterium exchangeable proton signal at δ 1.20 and

Table - Yields and melting points of **5a-d**, **7a-d**, and **9a-d**.

Starting material No.	Substituent R^1	Products No.	Yield (%)	mp (^oC)
2a	C_6H_5	**5a**	90	125
3a	C_6H_5	**7a**	45	115
		9a	54	195
2b	p-MeC_6H_4	**5b**	96	146
3b	p-MeC_6H_4	**7b**	33	89
		9b	60	180
2c	p-ClC_6H_4	**5c**	88	132
3c	p-ClC_6H_4	**7c**	35	108
		9c	60	171
2d	p-$MeOC_6H_4$	**5d**	84	168
3d	p-$MeOC_6H_4$	**7d**	40	138
		9d	55	160

two olefinic signals at δ 5.00 (s) and 6.30 (s) in the ratio 2:1:1. The ^{13}C-nmr spectrum contained the carbonyl carbon at δ 191.23 (C_2) and the ring carbons at δ 164.50, 161.13 and 133.79 (C_4, C_5, C_7, C_8). The characteristic ir absorption band at 1750 cm^{-1} confirmed the presence of -O-CO-NH- moiety in **7a**. Finally the molecular ions of **5a** and **7a** appeared at

m/e 277 and 278 respectively in their mass spectra. Based on these spectral data **5a** and **7a** were assigned the structures: 4,7-diphenyl-1,3,6-trihydro-1,3,6-triazocin-2-one and 3,6-dihydro-5,8-diphenyl-1,3,6-oxadiazocin-2-one respectively.

2H-Azirines **1b-d** reacted with CSI in an analogous manner and gave the azocine derivatives **5b-d**, **7b-d** and pyrazines (**9b-d**). The yields and melting points of all these compounds are collected in the table.

EXPERIMENTAL

Reaction of CSI with 2H-azirine

2H-Azirine (**1a**[3]) (0.468 g, 0.004 mol) was treated with CSI (0.36 ml, 0.004 mol) and chromatographed according to the reported[2] procedure, gave **2a** (0.25 g, 53%), mp. 95 °C and **3a** (0.16 g, 34%), mp. 105 °C.

Hydrolysis of **2a** (Preparation of **5a**)

The cycloadduct (**2a**) (0.15 g) was dissolved in acetone-water (20 ml, 9:1) and cooled to 0 °C. Aqueous KOH solution (5%) was added slowly until the solution became neutral. It was then diluted with water (10 ml) and extracted with dichloromethane (3x20 ml). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was flash chromatographed (silica-gel). Elution with ether-acetone (1:1) furnished **5a**

(0.1 g, 90%), crystallized in dichloromethane-petroleum ether (1:1), mp. 125 °C, ir (KBr), ν_{max}: 3300-3200, 3100, 2840, 1690, 1600, 1230, 770, 710 cm^{-1}; ms, m/e: 278 (M^++1, 10), 277 (M^+, 16), 173 (29), 159 (17), 121 (90), 103 (20), 101 (21), 77 (40), 59 (75), 43 (100); ^{1}H-nmr ($CDCl_3$), δ: 3.05 (b, 2H), 5.15 (s, 1H), 6.30 (s, 1H), 7.10-7.90 (m, 10H), 10.15 (s, 1H); ^{13}C-nmr [$(CD_3)_2SO$], δ: 193.00 (C_2), 155.01, 133.13 (C_4, C_5, C_7, C_8), 129.06, 128.65, 128.37, 128.17, 127.44, 127.23, 126.05, 124.91, 124.00 (phenyl carbons); Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.64; H, 5.41; N, 15.16; Found: C, 73.40; H, 5.36; N, 15.10.

Hydrolysis of **3a** (Preparation of **7a**)

Compound **3a** (0.1 g) was hydrolysed according to the above given procedure. Compound **7a** (0.033 g, 45%) was obtained as a precipitate on trituration of the organic extract with petroleum ether (40-60 °C). The mother-liquor on evaporation gave 2,5-diphenylpyrazine[2] (**9a**) (0.035) g, 54%). Compound **7a** was recrystallized from petroleum ether-dichloromethane (1:1), mp. 115 °C; ir (KBr), ν_{max}: 3400, 3080, 2960, 1750, 1610, 1460, 1240, 940, 760, 710 cm^{-1}; ms, m/e: 279 (M^++1, 4), 278 (M^+, 25), 247 (8), 232 (41), 220 (13), 176 (15), 173 (25), 160 (17), 145 (25), 116 (16), 105 (100), 103 (36), 77 (50), 51 (20), 44 (10), 43 (15); ^{1}H-nmr ($CDCl_3$), δ: 1.20 (s, 2H), 5.00 (s, 1H), 6.30 (s, 1H),

7.00-7.90 (m, 10H); ^{13}C-nmr ($CDCl_3$), δ: 191.23 (C_2), 164.50, 161.13, 133.79 (C_4, C_5, C_7, C_8), 129.11, 128.87, 128.68, 128.24, 127.97, 127.25, 127.02, 126.35, 125.04, 124.40, 124.05 (phenyl carbons); Anal. Cacd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.08; N,10.07; Found: C, 73.24; H, 5.30; N, 10.02.

2H-Azirine (**1a**) (0.234 g, 0.002 mol) was treated with CSI (0.18 ml, 0.002 mol) at -78-0 °C, followed by hydrolysis at 5 °C (without isolating **2a** and **3a**) gave triazocinone **5a** (0.095 g, 47.5%), oxadiazocinone (**7a**) (0.05 g, 25%) and 2,5-diphenylpyrazine (**9a**) (0.02 g, 10%). Satisfactory spectral and analytical data were obtained for compounds **5b-d**, **7b-d**, and **9b-d**.

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