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CYCLIZATION OF CHLOROSULFONYL ISOCYANATE WITH PHENYLHYDRAZONES: A SYNTHETIC ROUTE TO TRIAZINONOXATHIAZINEDIOXIDES AND TRIAZINONES

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Abstract : A convenient synthetic route is reported for the preparation of aroyl substituted triazinones and triazinonoxathiazinedioxides by the interaction of chlorosulfonyl isocyanate and phenylhydrazones (derived from acetylacetone, 1-benzoylacetone and dibenzoylmethane).

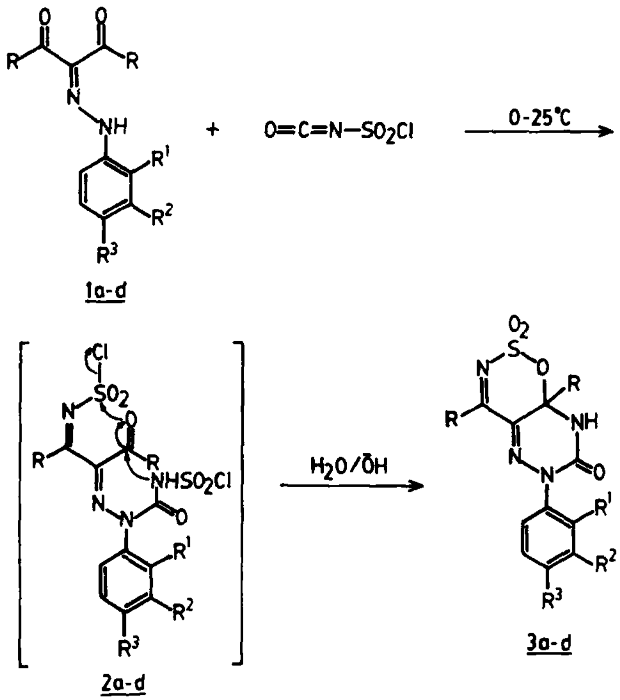
Chlorosulfonyl isocyanate (CSI, O=C=N-SO_2-Cl) has been extensively used as a reagent for the synthesis of many heterocycles[1,2]. Thus CSI reacts with 2-aminoacetophenones and 2-aminobenzophenones to give the corresponding heterocycles, viz., quinazolinones[3], while acetophenones and benzophenones under similar experimental conditions furnish the chlorosulfonylimino derivatives[4,5]. We carried out the reaction of 3-phenylhydrazono-2,4-pentadione ($(Ac)_2$C=N-NHPh)[6,7] with CSI and obtained an unexpected bicyclic product, **3a.** While on the other hand, a monocyclic product was obtained when 3-benzoyl-3-phenylhydrazono-2-acetone or phenylhydrazonodibenzoylmethane, was treated with CSI.

RESULTS AND DISCUSSION

Phenylhydrazones **1a-d**, derived from acetylacetone, underwent a smooth reaction with CSI at 0-5°C to give **3a-d** in 35-46% yield. The mass spectral fragmentation pattern (Table I) of these products indicates that they are formed by the insertion of $-SO_2N-$ and -CONH-moieties from CSI to **1a-d**. The ir absorption bands of **3a** (3500, 1698, 1593, 1362, 1168, 1092 cm^{-1}) confirmed the presence of -CONH-, C=N, and $-SO_2-$ functions in the molecules. Its ^{1}H-nmr spectrum showed two singlets (of three protons each) at δ 2.05 and 2.5 corresponding to the two methyl groups. Compounds **3b-c** showed identical spectral characteristics (Table I). Based on their spectral and analytical data, these were assigned the structure: 4,8a-dimethyl-6-phenyl-5,6,8-triazin-(8H)-7-one-1,2,3--oxathiazine-2,2-dioxides.

The formation of **3a-d** can be rationalized as depicted in Scheme I. Thus a bimolecular addition of CSI to I, produced **3**,through the intermediacy of **2**. The enhanced reactivity of the acetyl moiety of **1** towards CSI is responsible for the formation of 1:2 rather than 1:1 cycloadducts. The physical, spectral and analytical data of the products **3a-d** are collected in Table I.

It is interesting to note, however, that the phenylhydrazones **4a** and **4b**, derived from 1-benzoylacetone, on reaction with CSI



1a-d

2a-d

3a-d

1a-3a	$R = CH_3$, $R^1 = R^2 = H$, $R^3 = Cl$
1b-3b	$R = CH_3$, $R^1 = R^2 = R^3 = H$
1c-3c	$R = CH_3$, $R^1 = R^3 = H$, $R^2 = Br$
1d-3d	$R = CH_3$, $R^1 = R^2 = H$, $R^3 = CH_3$

SCHEME-I

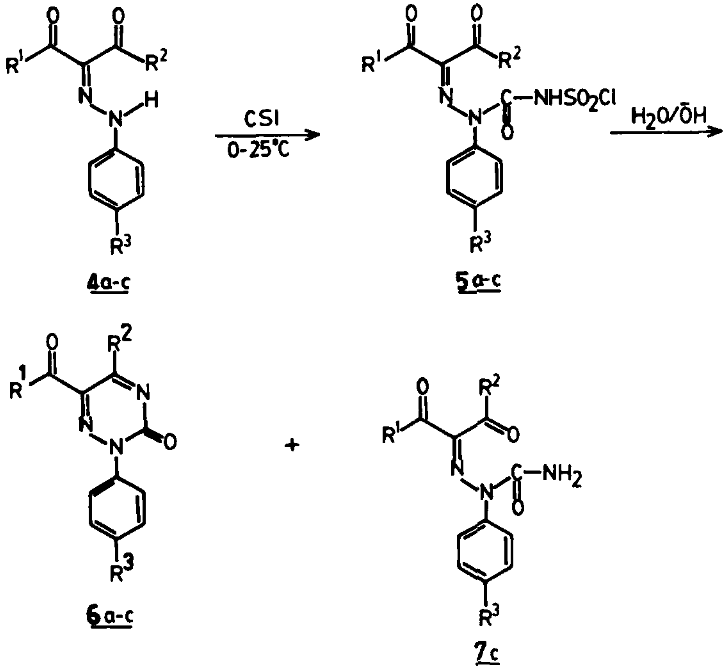
gave the 1:1 cycloadducts **6a** and **6b** in 75 and 65% yields respectively. The spectral and analytical data (Table II) of 6a-b confirmed the structure as 5-benzoyl-6-methyl-3-phenyl-1,3,4-triazin-2-ones. In an analogous manner (vide supra) the phenylhydrazone **4c** derived from dibenzoylmethane, on reaction with

TABLE I

Product No.	Yield %	mp °C	Analytical data		Spectral data		Mass m/e
			Calcd.	Found	ir cm^{-1}	pmr δ	
3a	46	175	$C_{12}H_{11}ClN_4O_4S$ C;42.05 H;3.23 N;16.34	 41.81 3.01 16.53	3500(b) 1698(CONH) 1593(C=N), 1362,1168, 1091(SO_2)	2.05(s,3H), 2.5 (s,3H), 5.9(b,NH,1H) 7.3(m,4H),	342(M^+),299(M^+-CONH), 294(M^+-SO), 278(M^+-SO_2), 262(M^+-SO_3), 237(M^+-MeCNSO$_2$), 125(ClC_6H_4N), 111(ClC_6H_4), 64(SO_2), 43(CONH)
3b	35	152	$C_{12}H_{12}N_4O_4S$ C;46.74 C;3.92 N;18.17	 46.56 3.72 18.02	3450(b), 1695(NHCO), 1598(C=N), 1370,1168, 1091(SO_2)	1.7(s,3H), 2.4(s,3H), 5.8(b,NH,1H), 7.5(m,5H)	308(M^+),265(M^+-CONH), 244(M^+-SO_2), 228(M^+-SO_3) 203(M^+-MeCNSO$_2$), 91(C_6H_5N),77(C_6H_5), 64(SO_2),43(CONH)
3c	44	155	$C_{12}H_{11}BrN_4O_4S$ C;37.14 H;2.85 N;14.44	 37.62 2.75 14.29	3460(b), 1700(CONH), 1600(C=N), 1390,1370, 1140, 1060(SO_2)	1.85(s,3H), 2.5(s,3H), 3.9(s,1H), 7.5(m,4H)	344(M^+-CONH), 339(M^+-SO) 323(M^+-SO_2), 307(M^+-SO_2Br), 282(M^+-MeCNSO$_2$), 198(BrC_6H_5NCO), 156(BrC_6H_4),64(SO_2), 43(CONH)
3d	45	138 -40	$C_{13}H_{14}N_4O_4S$ C;48.44 H;4.37 N;17.38	 48.21 4.24 17.48	3500(b), 1700(CONH) 1608(C=N), 1360,1165, 1090(SO_2)	1.65(s,3H), 2.35(s,6H), 5.7(b,NH,1H), 7.3(m,4H0	322(M^+),279(M^+-CONH), 274(M^+-SO), 258(M^+-SO_2), 242(M^+-SO_3), 217(M^+-MeCNSO$_2$), 105($CH_3C_6H_4N$), 91($CH_3C_6H_4$), 64(SO_2),43(CONH)

TABLE II

Product No.	Yield %	mp °C	Analytical data Calcd.	Found	Spectral data ir cm^{-1}	pmr δ	Mass m/e
6a	75	126	$C_{17}H_{12}ClN_3O_2$ C;62.68 H;3.71 N;12.89	 62.54 3.51 12.73	3060,2920, 1799,1671, 1600(C_6H_5CO, CON,C=N)	2.6(s,3H), 7.2-7.8 (m,9H)	325(M^+),297(M^+-CO), 282(M^+-CONH), 157(M^+,ClC_6H_4CON_2H), 138(M^+,$(C_6H_5)_2$Cl), 125(C_6h_4ClN), 111(C_6H_4Cl), 110(M^+-$(C_6H_4)_2$COCl), 105(C_6H_5CO)
6b	60	114	$C_{17}H_{13}N_3O_2$ C;70.09 H;4.49 N;14.42	 69.91 4.36 14.46	3058,2922, 1699,1680, 1595(C_6H_5CO, CON,C=N)	2.6(s,3H), 7.5(m,10H)	291(M^+),263(M^+-CO), 248(M^+-CONH), 105(C_6H_5CO),76(C_6H_5)
6c	40	230	$C_{22}H_{14}ClN_3O_2$ C;68.13 H;3.63 N;10.83	 68.31 3.53 10.65	3066,1695, 1667,1598, 1566(C_6H_5CO, CON,C=N)	7.3-8.3 (m,14H)	387(M^+),344(M^+-CONH), 200(M^+-C_6H_5ClC_6H_4), 157(M^+-ClCO$(C_6H_5)_2$), 105(C_6H_5CO)
7c	55	140	$C_{22}H_{16}ClN_3O_3$ C;65.10 H;3.97 N;10.35	 64.97 3.75 10.52	3450,3091, 1653,1609, 1594,1502, (C_6H_5CO, $CONH_2$,C=N)	7.5(m,14H), 12.95 (s,2H,NH)	405(M^+),387(M^+-H_2O), 362(M^+-CONH), 105(C_6H_5CO),77(C_6H_5)



4a-6a R^1 = Ph , R^2 = CH_3 , R^3 = Cl
4b-6b R^1 = Ph , R^2 = CH_3 , R^3 = H
4c-7c R^1 = R^2 = Ph , R^3 = Cl

SCHEME-II

CSI gave 5-benzoyl-3,6-diphenyl-1,3,4-triazin-2-one 6c and the N-carbamoyl derivative 7c. (Scheme II).

The initially formed 1:1 adduct of CSI and 4c has been isolated and characterized. It showed ir absorption bands at 3183 (-CONH-SO_2-), 1695, 1666 (C_6H_5CO, -CONH-), 1564 (C=N), 1364, 1198, 1016 cm^{-1} (SO_2Cl-) cm^{-1} which are consistent with the assigned structure. The ^{1}H-nmr spectrum of **5c** showed the -NH- proton signal at δ 5.9 and aromatic protons at 7.5. Its mass fragmentation pattern (m/z: 420 (M^+-SOCl), 404 (M^+-SO_2-Cl) 390 (M^+-NSO_2-Cl), 387 (M^+-SO_3HCl) is in good agreement with the assigned structure. The intermediate compounds **5a** and **5b** were not isolable due to their instability and hygroscopic nature. However, their structures can be postulated to be similar to that assigned for **5c**. The carbamoyl derivative, **7c**, constitute the major component (55%) of the reaction mixture of CSI and **4c** and arises due to the fact that benzoyl carbon does not favour the intramolecular cyclo-condensation.

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fisher-Johns melting point apparatus. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer. ^{1}H-nmr spectra were run on a Bruker WP-80 (80 MHz) spectrometer. Mass specture were taken on a Jeol JMS-300D mass spectrometer. The elemental analyses were carried out in a Coleman automatic carbon, hydrogen, nitrogen analysers. Compounds **1a-d** and **4a-c** were prepared according to the literature methods[6,7].

GENERAL REACTION PROCEDURE (3a-d, 6a-c, 7c)

To a stirred solution of 3-p-chlorophenylhydrazono-2,4-pentadione **1a** (0.476 g, 0.002 mol) in dry dichloromethane (20 ml), at 0°C, was added CSI (0.18 ml, 0.02 mol) in the same solvent (5 ml) for a period of ten minutes. Stirring was continued for thirty minutes at 0°C and twelve hours at room temperature ($\approx$25°C). Water (10 ml) was added and the dichloromethane layer was separated. An orange red semi-solid (0.75 g) was obtained, after removal of the solvent under diminished pressure. This semi-solid was dissolved in acetone-water (20 ml, 9:1) and neutralized with 5% aqueous KOH solution. The aqueous solution thus obtained was diluted with water (20 ml) and extracted with dichloromethane (3x20 ml). The combined extracts were washed with water and dried (Na_2SO_4). It was concentrated (2 ml) under reduced pressure and on trituration with petroleum ether (40-60°C) gave **3a** (0.310 g, 46%) mp 175°C, as orange red solid. The mother liquor on evaporation gave the unreacted starting material **1a**. (0.26 g).

The intermediate compound, **5c**, was isolated by concentrating the reaction mixture of CSI and **4c** followed by trituration with petroleum ether (40-60°C). The triazinone **6c** was easily separable from the associated N-carbamoyl derivative by suspending it in hot methanol. The triazinone was left as an insoluble residue.

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