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SYNTHESIS AND REACTIONS OF SOME NEW DERIVATIVES OF C-SULFONYLDITHIOFORMATES AND RELATED COMPOUNDS.

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ABSTRACT

*The prepared C-sulfonyldithioformates 3 reacted with SO_2Cl_2 to give the corresponding a-chlorosulfenyl chloride **4**, which in turn gave different products with nucleophiles **5-9**, among which the thiocarbonyl-S-imide **9**. These S-imides **9a,b** on treatment with SO_2Cl_2 afforded only the dichloromethane derivative **10**. Diels-Alder reaction of **3a-e** with 2,3-dimethyl-1,3-butadiene led to the corresponding Δ^3-dihydrothiopyrans **11**.*

DISCUSSION

In continuation of our work on C-sulfonyldithioformates 3[1,3], three new derivatives together with two known analogous compounds[2] were prepared according to eqn.(1) by two-phase reaction between aqueous sulfinate anions **1** and chlorodithioformates **2** [4] in benzene with tetrabutylammonium hydrogen sulfate as a phase tranfer catalyst.

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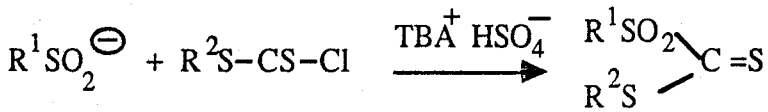
* known compounds.

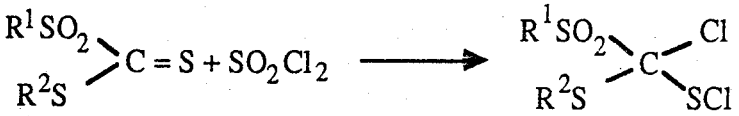


(1)

1 **2** **3**

3	R^1	R^2
a	4-$CH_3C_6H_4$	$(CH_3)_2CH$
b	4-ClC_6H_4	4-ClC_6H_4
c	C_6H_5	4-ClC_6H_4
d*	C_6H_5	C_6Cl_5
e*	4-$CH_3C_6H_4$	C_6H_5

Chlorinationn of C-sulfonyldithioformates **3b,d** with excess SO_2Cl_2 at room temperature formed the corresponding α-chloromethanesulfenyl chloride **4**[5,6] eqn.(2)



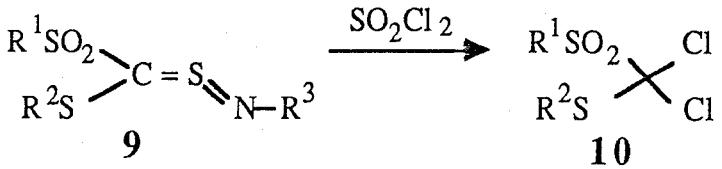
(2)

4

4	R_1	R^2
a*	C_6H_5	C_6Cl_5
b	4-ClC_6H_4	4-ClC_6H_4

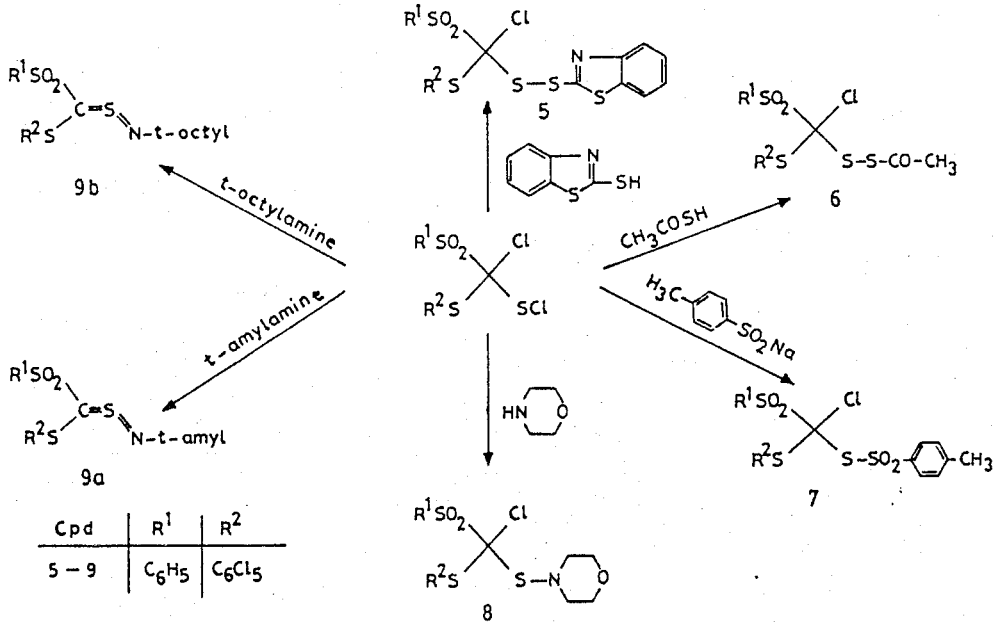
A further study on the chemistry of sulfenyl chloride led upon reactions with various nucleophiles[7], for instance, when (phenylsulfonyl) (pentachlorophenylthio) chloromethanesulfenyl chloride **4a** was allowed to react with 2-mercaptobenzothiazole afforded the unsymmetrical disulfide, [α–Chloro (phenylsulfonyl) (pentachlorophenylthio) methyl] 2-benzothiazolyl disulfide **5.** Also wih thioacetic acid it gave [α–Chloro-(phenylsulfony) (pentachlorophenylthio) methyl] acetyl disulfide **6.** With p-toluene sulfinic acid sodium salt , S–[Chloro(phenylsulfonyl) (pentachlorophenylthio)methyl] p-toluene sulfonate **7** was obtained. The same sulfenyl chloride **4a** was derivatized with secondary hetererocydic amines such as morpholine [6] to form the corresponding sulfenamide, α–Chloro–[(phenylsulfonyl) (pentachlorophenylthio)] methanesulfenomorpholide **8** , while with t–alkylamines such as t–octylamine and t-amylamine[10,11] it gave, C-Sulfenyldithioformates S-[N-(t-alkyl)imides] **9a-b** (cf. Scheme 1).

Chlorination of **9a-b** by means of SO_2Cl_2 at room temperature afforded only (Pentachlorophenylthio) dichloromethyl phenyl sulfone **10** [6,12] according to (3).



(3)

Cpd.	R^1	R^2	R^3
9a	C_6H_5	C_6Cl_5	t-octyl
9b	C_6H_5	C_6Cl_5	t-amyl
10	C_6H_5	C_6Cl_5	——

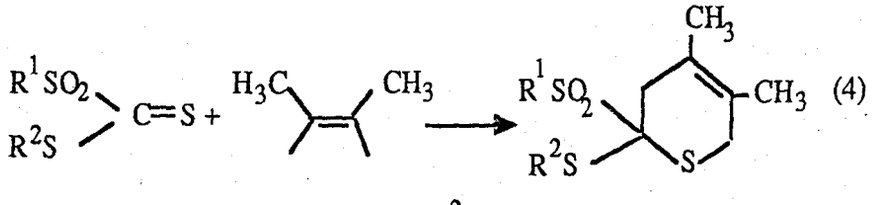


Cpd	R^1	R^2
5 – 9	C_6H_5	C_6Cl_5

Scheme 1

The corresponding dienophilic properties of c-sulphonyl-dithioformates have been demonsrated by Diels-Alder reactions with 2,3-dimethyl-1,3-butadiene. Since **3a-e** contains an electron depleted thiocarbonyl group and thus should be potent dienophiles, and the work to be presented here fully describe this expectation. When 2,3-dimethyl-1,3-butadiene was added to a solution of **3a-e** in CH_2Cl_2 at room temperature, the reaction is completed within few minutes as judged by the discharge of the violet colour of **3**, with the formation of Δ^3-dihydrothiopyrans **11**[8], as shown by eqn.(4).

The above compound **11** decomposes rapidly on standing at room temperature and should be used immediately.



(4)

11

11	R^1	R^2
a	4-$CH_3C_6H_4$	$(CH_3)_2CH$
b	4-ClC_6H_4	4-ClC_6H_4
c	C_6H_5	4-ClC_6H_4
d	C_6H_5	C_6Cl_5
e	4-$CH_3C_6H_4$	C_6H_5

Table 1. Spectral data

Cpd.	^{1}H NMR ($CDCl_3$) δ (ppm)	IR (KBr) (Cm^{-1})
3a	1.4(d, 6H), 2-45(s, 2H), 3.75(septet,1H) 7.33(d, 2H),7.9(d, 2H).	ν_{SO_2} 1160 1320 ν_{CH} 2850 2950
3b	7.3(d,2H), 7.45(d, 2H), 7.55(d, 2H), 8.0(d, 2H).	ν_{SO_2} 1150 1330 $\nu_{C=S}$ 1090
3c	7.25(d, 2H), 7.4(d, 2H), 7.6 (m, 2H),7.7(m, 1H),8.05(d, 2H).	ν_{SO_2} 1145 1335 $\nu_{C=S}$ 1040
4b	7.35(d, 2H), 7.45(d, 2H), 7.6(d, 2H), 8.05(d, 2H).	ν_{SO_2} 1150 1330
5	7.35(m, 3H), 7.7(m, 4H), 8.15(d, 2H).	ν_{SO_2} 1155 1320
6	2.4(s, 3H), 7.5(t, 2H), 7.8(d, 1H), 8.1(t, 2H).	ν_{SO_2} 1150 1340 $\nu_{C=O}$ 1720
7	2.45(s, 3H), 7.6(m, 4H), 7.75(m, 1H), 8.0(dd, 4H).	ν_{CH_2} 1155 1330
8	3.35(m, 4H), 3.65(m, 4H), 7.6(m, 2H), 7.7(m, 1H), 8.15(d, 2H).	ν_{SO_2} 1160 1340 ν_{CH} 2860 2920 2960
9a	0.95(t, 3H), 1.4(s, 6H), 1.75(q, 2H), 7.5(t, 2H), 7.55(t, 1H), 7.9(d, 2H).	ν_{SO_2} 1150 1340 $\nu_{S=N}$ 930
9b	1.2(s, 9H), 1.5(s, 6H), 1.7(s, 2H), 7.45(m, 2H), 7.6(m, 1H), 7.9(m, 2H).	ν_{SO_2} 1145 1345 $\nu_{S=N}$ 940
10	7.6(m, 3H), 7.95(d, 1H), 8.15(d, 1H).	ν_{SO_2} 1160 1340 ν_{C-Cl} 650
11a	1.5(d, 6H), 1.7(d, 3H), 1.9(s, 3H), 2.45(s, 3H), 2.75(m, 3H), 3.2(d, 1H), 4.65(septet, 1H), 7.25(d, 2H),7.55(d, 2H)	ν_{SO_2} 1156 1320
11b	1.75(s, 3H), 1.9(s, 3H), 2.8(m, 3H), 3.1(d, 1H), 7.6(d, 2H), 7.45(d, 2H), 7.25(dd, 4H.	ν_{SO_2} 1155 1320
11c	1.7(s, 3H), 1.8(s, 3H), 2.85(m, 3H), 3.2(d, 1H), 7.2(d, 2H), 7.5(d, 2H), 7.6(m, 2H), 7.7(m, 1H), 8.2(d, 2H).	ν_{SO_2} 1150 1330
11d	1.7(s, 3H), 1.75(s, 3H), 2.9(m, 3H), 3.1(d. 1H), 7.55(m, 2H), 7.65(m, 1H), 8.1(d, 2H).	ν_{SO_2} 1155 1340
11e	1.75(s, 3H), 1.85(s, 3H), 2.4(s, 3H), 2.9(m, 3H), 3.1(d, 1H), 7.35(m, 3H), 7.4(d, 2H), 7.55(d, 2H), 7.65(d, 2H).	ν_{SO_2} 1150 1330

The structure of all compounds was confirmed by ^1H NMR, IR, and microanalytical data (cf. Tables 1 and 2)

EXPERIMENTAL

C-Sulfonyldithioformates 3.

The two-phase mixture of the appropriate sodium sulfinate dihydrate **1** (0.01 mol), **2** (0.01 mol), 1.0 g. tetrabutylammonium hydrogen sulfate, 100 ml. benzene, and 100 ml. water was stirred at room temperature, and the progress of the reaction is checked by TLC (Merck silica gel, eluent ether/petroleum ether 1:5). When the reaction was completed the benzene phase was separated and washed with water (3 times), dried over anhydrous calcium chloride, and evaporated in vacua. The remained oily red residue was solidified on addition of ether/petroleum ether (1:1) and cooling. The recrystallization was carried out as shown in Table 2.

a-Chloromethanesulfenyl Chloride 4b

To a stirred solution of the appropriate **3** (5 mmol) in 30 ml. carbon tetrachloride was added SO_2Cl_2 (8 mmol) and stirring was continued at room temperature until the violet colour of **3** disappears. The solven was evaporated under reduced prossure, and the solid formed was triturated with ether 20 ml. Recrystillization was done as shown in Table 2.

α–Chloromethane disulphide 5,6.

Equimolecular ammounts of the appropriate thiol and α–chloromethane-sulfenyl chloride **4** were stirred in ether (50 ml.) at room temperature for 24 hours. The solid formed was callected by filtration and recrystallized from the suitable solvent (cf. Table 2).

α–Chloromethyl-S-p-toluene sulfonate 7.

To a stirred solution of **4** (1.0 mmol) in benzene (40 ml.) was added p-toluene sodium sulfinate (1.0 mmol), and stirring was continued at room temperature for 2 hours. The solvent was distilled off under reduced pressure and ether (10 ml.) was added and evoled. The solid formed was collected by filtration and recrystallized (cf. Table 2).

α–Chloro-[(phenylsulfonyl)(pentachlorophenylthio)] methanesulfeno-morpholide 8.

A stirred solution of **4a** (2.7g., 5 mmol) in 50 ml. $CHCl_3$ was treated with excess morpholine (8.6 ml.,100 mmol) at room temperature. After the addition was complete, the reaction mixture was stirred for another 20 minutes. The formed salt was removed by filtration and the chloroform phase was washed with water (3 times), dried over anhydrous $CaCl_2$, and evaporated in vacuu. The residual oil was treated with ether and cooled. The solid precipitaled then recrystallized (cf. Table 2).

C-Sulphenyldithioformates thiocarbonyl S-imides 9.

To a stirred solution of **4a** (3 mmol) in 30 ml. chloroform was added dropwise the appropriate t-alkylamine (10 mmol) at room temperature. After the addition was complete, the reaction mixture was stirred for another 15 mins., the precipitated salt filtered off, and the chloroform phase was washed with water (3 times), dried over anhydrous $CaCl_2$, and evaponated in vacuu. The residue was triturated with 40 ml. petroleum ether with cooling whereupon the crude product crystallizes out. The recrystallization was carried out as shown in Table 2.

(Pentachlorophenylthio)phenyl sulfone 10.

To a stirred solution of **9** (0.001 mol.) in 50 ml. CCl_4, was added dropwise SO_2Cl_2 (0.01 mol), and stirring was continued at room temperature for an hour. The solvent was evaporated under reduced pressure till dryness. The solid formed washed with petroleum ether and recryotallized (cf.Table 1).

C-Sulphonyldithioformate–2,3–dimethyl–Δ^3–dihydro-thiopyrans 11.

A mixture of **3** (5 mmol) in 40 ml. dry ether and a large excess of 2,3-dimethyl-1,3-butadiene (20 mmol) was stirred at room temperature until the violet colour disappeared (5-15 mins). The ether was evaporated in vacuu and petroleum ether (20 ml.) was added. The solid formed was collected by filtration and recrystallized from proper solvent (cf. Table 2).

Table 2. Experimental data

Cpd.	Yield (%)	M.P.(C°) Solvent	Molecular formula (M. wt.)	Analysis Calc. / Found C	H	Cl	N	S
3a	40	43 ether / pet. ether	$CH_{11}H_{14}O_2S_3$ (274)	48.2 47.9	5.1 5.0	— —	— —	35.0 35.4
3b	70	124 pet. ether	$C_{13}H_8Cl_2O_2S_3$ (363)	43.0 42.6	2.2 2.5	19.6 19.3	— —	26.4 26.0
3c	65	109 ether	$C_{13}H_9ClO_2S_3$ (328.5)	47.5 47.9	2.7 2.2	10.8 11.0	— —	29.2 28.9
4b	80	127 CH_2Cl_2/ pet.ether	$C_{13}H_8Cl_4O_2S_3$ (434)	35.9 35.4	1.4 1.2	32.1 32.5	— —	22.9 22.0
5	80	185 CH_2Cl_2/ pet.ether	$C_{20}H_9Cl_6NO_2S_5$ (668)	35.9 36.1	1.3 1.5	31.9 31.6	2.1 2.0	24.0 23.3
6	60	114 pet. ether	$C_{15}H_8Cl_6O_3S_4$ (589)	32.9 32.5	1.4 1.1	36.2 37.0	— —	21.7 21.0
7	55	140 Acetonitrile	$C_{20}H_{12}Cl_6O_4S_4$ (657)	36.5 36.1	1.4 1.2	32.4 31.9	— —	19.5 19.2
8	75	194 CH_2Cl_2/ pet. ether	$C_{17}H_{13}Cl_6NO_3S_3$ (588)	34.7 35.1	2.2 2.1	36.2 35.8	2.4 2.1	16.3 16.9
9a	80	160 - 3 pet. ether	$C_{18}H_{16}Cl_5NO_2S_3$ (551.5)	39.3 39.7	2.9 2.8	32.2 32.1	2.5 2.4	17.4 17.0
9b	80	195 - 7 pet. ether	$C_{21}H_{22}Cl_5NO_2S_3$ (593.5)	42.5 42.7	3.7 3.1	29.9 30.2	2.4 2.1	16.2 15.9
10	60	155 pet. ether	$C_{13}H_5Cl_7O_2S_2$ (505.5)	30.9 31.1	1.0 0.5	49.2 48.9	— —	12.7 12.3
11a	30	88 ether / pet. ether	$C_{17}H_{24}O_2S_3$ (356)	57.3 57.5	6.7 7.2	— —	— —	27.0 26.3
11b	50	70 CH_2Cl_2/ pet. ether	$C_{19}H_{18}Cl_2O_2S_3$ (445)	51.2 51.1	4.0 3.7	16.0 15.5	— —	21.8 22.2
11c	55	81 ether / pet. ether	$C_{19}H_{19}ClO_2S_3$ (410.5)	55.5 54.1	4.6 4.5	8.6 9.1	— —	23.4 22.8
11d	55	90 ether / pet. ether	$C_{19}H_{15}Cl_5O_2S_3$ (548.5)	41.6 41.7	2.7 3.0	32.4 32.0	— —	17.5 17.0
11e	65	65 CH_2Cl_2/ pet. ether	$C_{20}H_{22}O_2S_3$ (390)	61.5 62.0	5.6 6.1	— —	— —	24.6 25.1

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تحضير وتفاعلات بعض المشتقات الجديدة منC-سلفونيل داى ثيو فورمات والمركبات المشابهة

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فى هذا البحث قد تم تحضير ثلاث مشتقات جديدة من المركب C-سلفونيل داى ثيو الفورمات علاوة على اثنين تم تحضيرهما مسبقا(٣). وبتفاعل بعض هذه المشتقات مع كلوريد السلفونيل أعطت مركبات α-كلورو سلفينيل الكلوريد المناظرة (٤) وقد أعطت هذه النواتج بدورها مركبات مناظرة مع النيوكليوفيلات المختلفة (٥-٩). ومن بينها المركبات S-أميدات التى تعطى بمعالجتها بواسطة كلوريد السلفونيل مشتقات ثنائى كلورو الميثان المناظرة (١٠) . أما تفاعل ديلز-ألدر مع مركبات C- سلفونيل داى ثيو فورمات فقد اعطى مركبات بالاضافة وتعرف بإسم Δ^3- داى هيدرو ثيو البيران (١١) . وقد تم التعرف على المركبات الناتجة باستخدام الرنين النووى المغناطيسى للبروتون والأشعة دون الحمراء بالإضافة الى التحليل الكمى.