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REACTION OF 2-DIALKYLAMINO-5-PHENYL-1,3-OXATHIOLIUM CATION WITH SULPHUR YLIDES[1]

KENTARO HIRAI,* HIROHIKO SUGIMOTO and TERUYUKI ISHIBA
Shionogi Research Laboratory, Shionogi & Co., Ltd., Sagisu, Fukushima-ku, Osaka 553, Japan

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Abstract—The reaction of 2-dialkylamino-5-phenyl-1,3-oxathiolium cation **1** with sulphur ylides **2** was investigated. The behavior of **1** was solvent-dependent. In CH_2Cl_2, carbamate ester **3** was obtained: in CH_3CN, the intermediate sulphonium salt **5**, which on hydrolysis gave **3**, was isolated. On the other hand, reaction in MeOH gave the diphenacyl derivative **6**. The reaction mechanism is discussed.

1,3-Oxathiolium cation **1** is a member of a 6π conjugated system with a positive charge on a five-membered ring. A C-2 carbon, which has the largest positive charge density, is bonded with three hetero atoms, leading to high reactivity toward a variety of nucleophiles.

We have investigated the behavior of **1** towards a number of nucleophiles. Active methylene compounds react with **1** in the presence of base to yield thiophene, 2-hydroxy-2,3-dihydrothiophene and 1,3-oxathiafulvene derivatives.[2] Primary amines act as nucleophiles toward **1** to afford thiazole, thiadiazine derivatives in addition to ring-opened products.[3] From this point of view, cation **1** is a versatile intermediate for the syntheses of many heterocyclic compounds.

In our continued studies on 1,3-oxathiolium cation **1**, we studied its reactivity toward sulphur ylides **2**. The reaction course was solvent-dependent. In aprotic solvent, the reaction product was carbamate ester derivatives **3**, and especially in CH_3CN, an intermediate **5** which lead to **3** on hydrolysis was isolated. In MeOH, diphenacyl sulphide derivative **6** was obtained. Evidence of the product structure was obtained from spectral data.

RESULTS

When cation **1a** reacted with ylide **2a** in methylene chloride for 2 h at room temperature, followed by subsequent hydrolysis of the organic layer, we obtained a product of the formula $C_{22}H_{21}NO_5S$ (**3a**), m.p. 150–151° after recrystallization from ethyl acetate. The NMR spectrum of **3a** in $CDCl_3$ showed the presence of piperidino (δ 3.64–3.25, 4H and 1.65–1.40, 6H), phenyl and benzoyl (8.10–7.80, 2H and 7.57–7.20, 8H), methylene (4.04), and methine (6.43) hydrogens. Apparently the dimethylsulphide moiety was lost. This was experimentally verified by the formation of **3a** upon reaction of **1a** with **2b** (62% yield). Table 1 summarizes the results.

The origin of the protons of **3a** can be deduced by examination of the NMR spectra of the reaction product of **1** with **2**. The NMR spectrum of product **3b** showed that a *p*-nitrophenyl group corresponded to the benzoyl group of product **3a**. Thus, the benzoyl group came from the ylide moiety. Furthermore, the reaction of cation **1b**, where the C-4 proton of **1a** is replaced by a phenyl group, with **2c** was carried out, giving **3c** which had no methine proton. This shows that the methine proton in **3a** is derived from cation **1a**. Thus, the remaining methylene protons must come from the ylide. **3a** contains three oxygen atoms per molecule. Its IR revealed the presence of two types of carbonyl bands at 1705 and 1672 cm^{-1}. It reacted with one mole of phenylhydrazine to form hydrazone **4**, which was identified by IR, NMR and analytical data. This indicates that the benzoyl-type carbonyl bond formed hydrazone and the other two oxygen atoms per molecule may constitute an ester bond. This was ascertained by the ^{13}C spectrum in $CDCl_3$, which showed a benzoyl carbonyl carbon at 193.8 ppm and the other type of carbonyl carbon at 152.1 ppm.

Among the mass spectra of **3**, that of **3b** unam-

Table 1. Reaction of cation **1** with ylide **2** in different solvents

1	R_1	R_2	R_3	X	2	R_4	R_5	Solv.	Prod.	R_1	R_2	R_3	R_4	M.p. (°C)	Yield (%)
a			H	HSO_4	a	H	Me	CH_2Cl_2	3a			H	H	150-151	65
a					b	H	Ph	CH_2Cl_2	3a	"		H	H		62
a					c	NO_2	Me	CH_2Cl_2	3b	"		H	NO_2	97-100	58
b			Ph	ClO_4	c			CH_2Cl_2	3c			Ph	NO_2	137-138	71
c			H	HSO_4					3d	"		H	H	132-134[a]	60
c					a			CH_3CN	5a	"				b	98
a					a			CH_3CN	5b					125-127[c]	19
c					d	Cl	Me	MeOH	6				Cl	80-81	32

[a] from 5a. [b] hygroscopic. [c] dec.

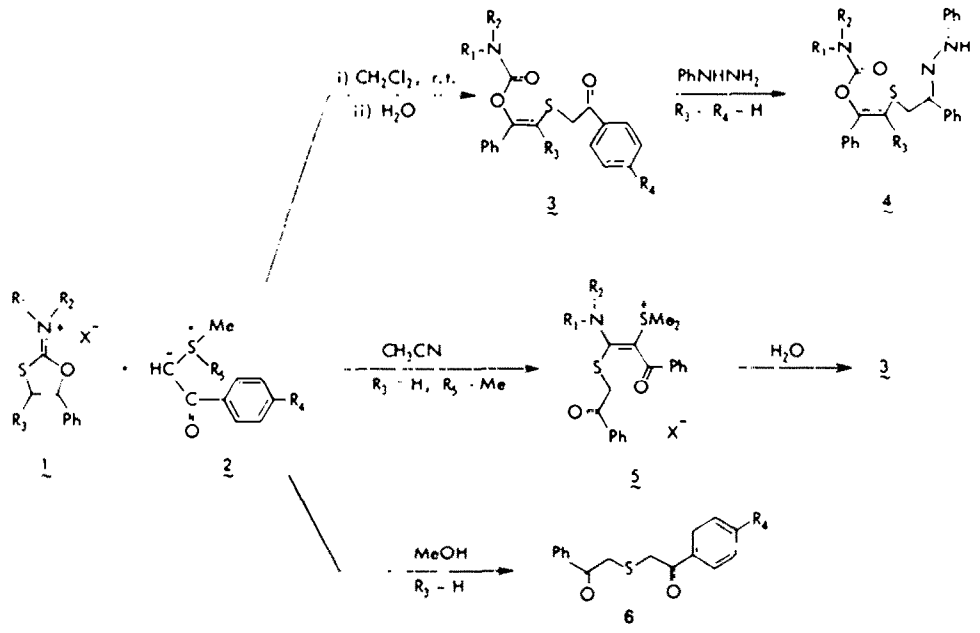

Chart 1.

biguously revealed the dependence of fragmentation on the chamber temperature, as shown in Fig. 1. At low chamber temperature (about 140°), the mass spectrum appears to show the superposition of 2-oxo-5-phenyl-1,3-oxathiole **12**[4] and piperidine, whereas at high chamber temperature (about 210°), it seems to include yet unsynthesized 4-phenyl-2-piperidino-1,3-dioxolium cation **13** (see Experimental). Thus, we concluded that the two oxygen atoms of **3** are incorporated in a carbamate bond.

These results indicated that **3a** is *cis*-*O*-1-phenyl-2-benzoylmethylthioethenyl *N,N*-piperidinocarbamate. The *cis* configuration was derived from mechanistic considerations.

We obtained the ketene-*S,N*-acetal type intermediate **5'** for the reaction of **1** with active methylene compounds or primary amines (the general reaction pathway is depicted in Fig. 2). In the case of ylide carbanion, the reaction course might follow the same pathway as that for the reaction of **1** with active methylene compounds. We tried to isolate the intermediate leading to **3**. The reaction of **1c** with **2a** in CH_3CN at −20° to 10° gave a colourless product which was very hygroscopic; its NMR spectrum showed that it was a sulphonium salt (**5a**, 98% yield).

Treatment of **5a** with water gave **3d** in 60% yield. To characterize the intermediate sulphonium salt more precisely, we reacted **1a** with **2a** in CH_3CN. Subsequent anion exchange of the initially formed hygroscopic salt (hydrogen sulphate) with 60% $HClO_4$ aq afforded a stable salt (**5b**). The NMR spectrum of **5b** in d_6-DMSO showed a dimethylsulphonium group (δ 3.05) and piperidino (4.27–3.57 and 1.90–1.73) and methylene (5.47), in addition to, benzoyl protons (8.13–7.30). Elementary analysis proved it was sulphonium perchlorate hydroperchlorate (19% yield).

To ascertain the carbamate formation by the hydrolysis of thiirenium cation as shown in Fig. 3, we reacted **1c** with **2d** in methanol to see whether or not methanolysis of the thiirenium cation intermediate takes place. The same conditions as in methylene chloride did not give the carbamate ester, but afforded many spots on TLC. Separation by column chromatography on silica gel with ether as an eluant gave a diphenacyl sulphide derivative **6** as the major product (32%); its structure was determined from spectral and analytical data.

DISCUSSION

The reaction of **1** with active methylene compounds proceeds *via* formation of a ketene-*S,N*-acetal intermediate **5'** or **5"** as shown in Fig. 2. By analogy, the reaction course of **1** and **2** in methylene chloride can be best explained by the route shown in Fig. 3.

We tried to isolate the intermediate in the above mechanism and obtained from the reaction of **1c** with **2a** in acetonitrile at −20–10°. Sulphonium salt **5a**, the hydrogen sulphate, was highly hygroscopic, but treatment of it with water in the absence of base gave the final product, **3d**, in 60% yield. Intermediate **5a** is a structural isomer of the initial adduct **7**, which has an acidic proton that can be easily extracted in the presence of excess ylide to give another ylide **8**. Ring-opening of the oxathiole ring with C RR substituent at the C-2 carbon has been experimentally established by previous works as shown in Fig. 2. Thus, the intermediate isolated was concluded to be **5a** and not **7**. Structural confirmation of **5** was obtained by isolating **5b**. Though ylide **2** is a well-known ambident nucleophile,[5] the formation of **5** supports the reactivity of **2** as a carbanion nucleophile.

Generally, isolation of the **7**-type intermediate is difficult for oxathiole derivatives having a CHRR group at the C-2 carbon in the presence of excess nucleophile (which acts as a base). However, for dithiolium cation **1'**, the dithiole ring-retained product can be isolated as shown in Fig. 2. 2-Dialkylamino-4-phenyl-1,3-dithiolium cation **1'** did not react with ylide **2a** under the same conditions as for cation **1**. On the other hand, reaction of 4-aryl-1,3-dithiolium cation **11** with ylide **2a** gave another type of ylide intermediate **8a**. Thus, the course for the formation of the sulphonium group-substituted ethylene intermediate **5** is reasonable. This class of compounds is generally a good precursor for the vinyl cation[6] and in

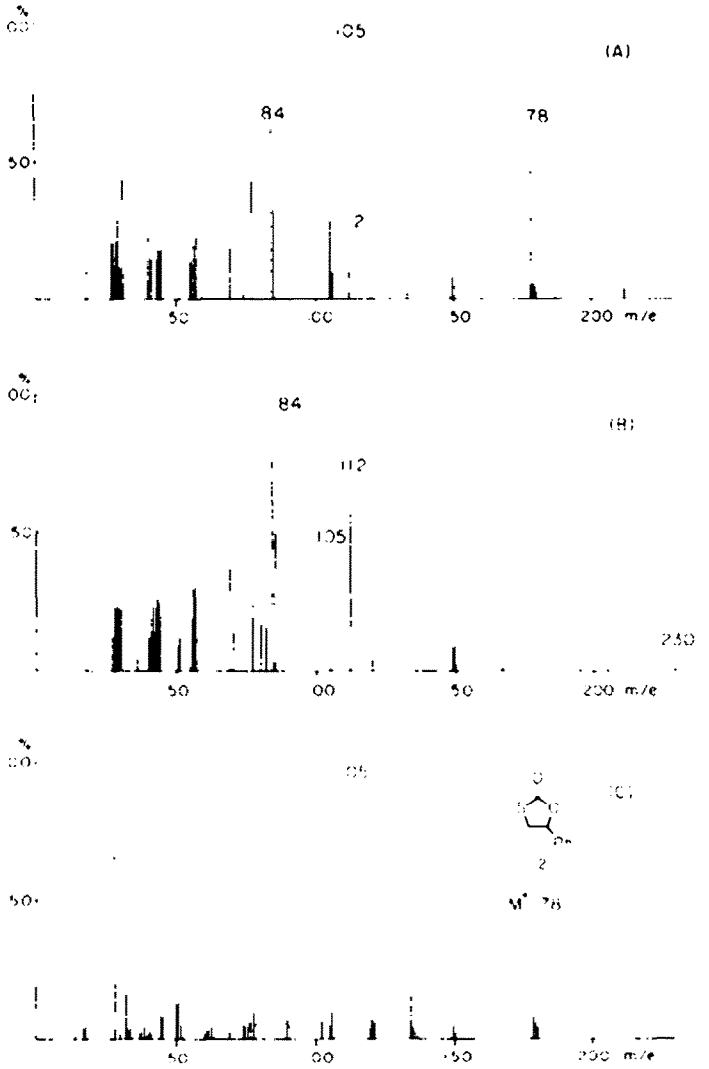

Fig. 1. Mass spectra of **3b** at low (A) and high (B) chamber temperatures. Spectrum (C) is that of an authentic sample of **12**.

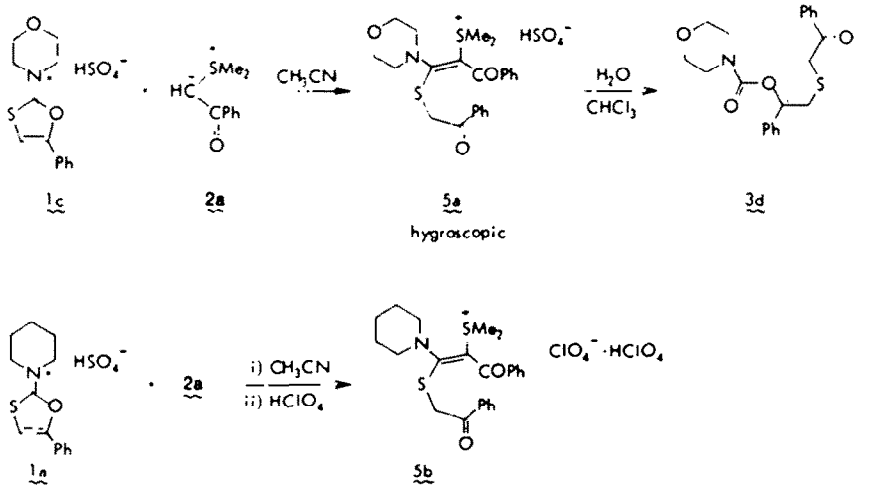

Chart 2.

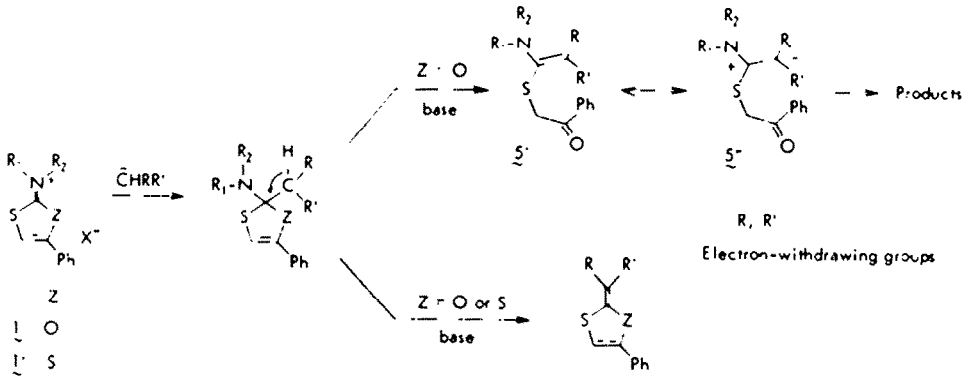

Fig. 2. General reaction course of cations 1 and 1' with active methylene compounds.

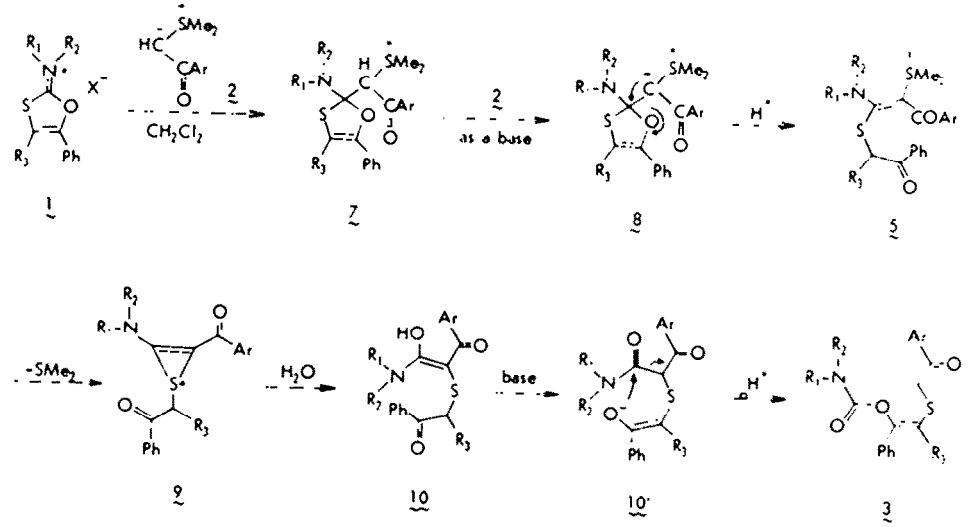

Fig. 3. Reaction course of 1 with 2 in CH_2Cl.

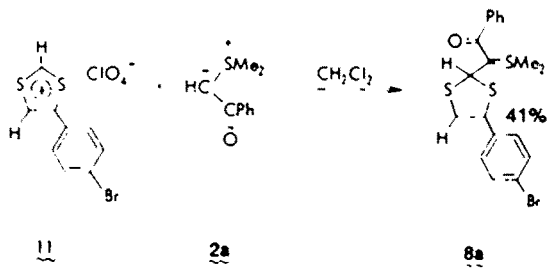

Chart 3.

the case of **5**, intramolecular attack of the sulphur atom to eliminate dimethyl sulphide gives thiirenium cation **9**.[7] Many studies have been reported on the solvolysis of thioether,[8] in which the thiirenium cation is an intermediate. And the addition of arenesulphenyl chlorides of alkyne has been postulated to involve a transition state leading to thiirenium cation. The products are formed by anti stereospecific and nonregiospecific addition of nucleophiles.[9] It is well known that the formation of thiirenium cation from vinyl sulphide is an S_Ni type reaction with the anchimeric assist of a *trans* β-sulphur atom.

Rotational isomerization about the double bond of intermediate **5** is easily equilibrated because of the large contribution of the polar structure as shown in Fig. 2 (**5'** or **5"**). Thus the configuration of **5** has been assumed to have little affect on its transformation into thiirenium cation **9**. Furthermore, **9** has dialkylamino and benzoyl groups on two ethylenic carbons and the contribution of the polar structure with respect to the enaminoketone moiety, which is similar to **5'**, increases the stability of **5** and makes easy the regiospecific addition of water at the piperidino-attached carbon. Stabilization of cyclobutadiene system due to the push-pull effect of electron-donating and electron-withdrawing groups attached to it has been described.[10]

Hydrolysis of the thiirenium cation gave *C*-carbamoyl diphenacyl sulphide **10**. The base promoted migration of the carbamoyl group from C to O giving the final product (**3a**). The rearrangement was facilitated by the presence of the electron-withdrawing group (benzoyl) at position β to the carbamoyl-substituted carbon. The same type of rearrangement of the carbethoxy group from C to O has been described by Lichtenthaler.[11]

The mass spectra at different chamber temperatures can be rationalized by the formation of intermediates **12** and **13** at each temperature. The spectrum at the lower

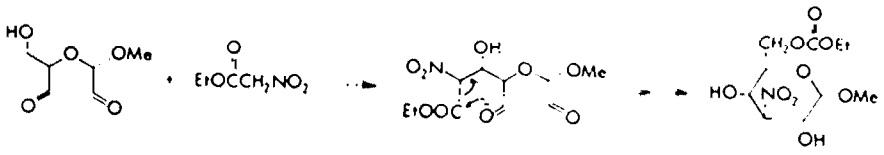

Chart 4.

temperature is similar to that of **12** in addition to piperidine. For both temperatures, fragmentation takes place at the C–S bond, which has the smallest bond energy in the molecule. Formation of intermediates **12** and **13** can be explained as follows. The existence of *m/e* 112 or the piperidino-carbamoyl cation associated with the presence of urethane ketone in the ^{13}C spectrum is the key evidence of water cooperation or formal attack of water at the C-2 carbon of the oxathiole ring.

In methanol, the reaction can be best accounted for in terms of the methanolysis of thiirenium cation **9** as shown in Fig. 4. The initial solvolysis product **14** has an electron-withdrawing group on one carbon of the double bond, and an electron-donating group on the other carbon. Hence the large contribution of the polar structure to its resonance hybrid as depicted in Fig. 2. Further attack of two molecules of methanol give carbamide acetal and product **6**. Methanol attack of intermediate **15** results in bond scission of C_α–C_β due to the presence of the benzoyl group. Carbamide acetal formation has been described by Meerwein.[12]

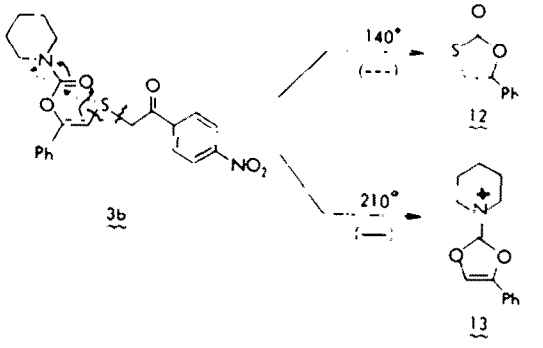

Chart 5.

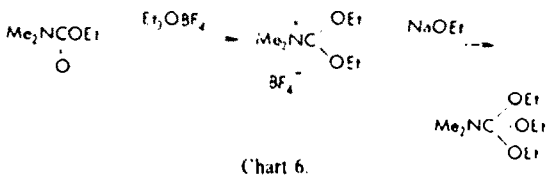

Chart 6.

EXPERIMENTAL

M.ps are uncorrected. The UV spectra were measured with a Hitachi EPS-2 spectrophotometer, IR spectra in KBr with a JASCO DS-403G spectrometer, NMR spectra on a Varian A-60 instrument with TMS as an internal standard, ^{13}C spectra using a Varian NV-14 FT NMR spectrometer, mass spectra on a Hitachi RMU-6E spectrometer, and double focus mass spectra on a Hitachi RMU-8GN spectrometer with an ionizing voltage of 70 eV.

Preparation of 2-dialkylamino-5-phenyl-4-substituted-1,3-oxathiolium cation **1**. Cation **1** was prepared according to the general procedure described by Hirai and Ishiba.[11]

Dimethyl or methylphenylsulphonium phenacylide **2**. Syntheses of ylides **2** are documented by Trost and Melvin.[14]

cis-O-1-Phenyl-2-benzoylmethylthioethenyl N,N-piperidinocarabamate **3a**. A mixture of 1.38 g of **1a** and 1.50 g of **2a** in 20 ml of CH_2Cl_2 was stirred for 2 h at room temp. The yellow mixture was washed with water and the organic layer was separated, dried and concentrated. The tarry residue was triturated with ether. Recrystallization from AcOEt yielded 0.995 g (65%) of **3a**: m.p. 150–51°; IR (KBr, cm^{-1}) 1705 ($\nu_{C=O}$, urethane), 1672 ($\nu_{C=O}$), 1597 ($\nu_{C=C}$); NMR ($CDCl_3$) δ 8.10–7.80 (m, 2H, Ar), 7.57–7.20 (m, 8H, Ar), 6.43 (s, 1H, methine), 4.04 (s, 2H, CH_2), 3.64–3.24 (m, 4H, piperidino), 1.65–1.40 (m, 6H, piperidino); UV (EtOH) λ_{max} nm (log ϵ), 225(4.21), 231(4.25), 248(4.22), 287(4.31), 343(3.14); ^{13}C spectrum ($CDCl_3$). Partial signal assignment was made with the aid of SFORD as shown below. The carbons with • are 134.63

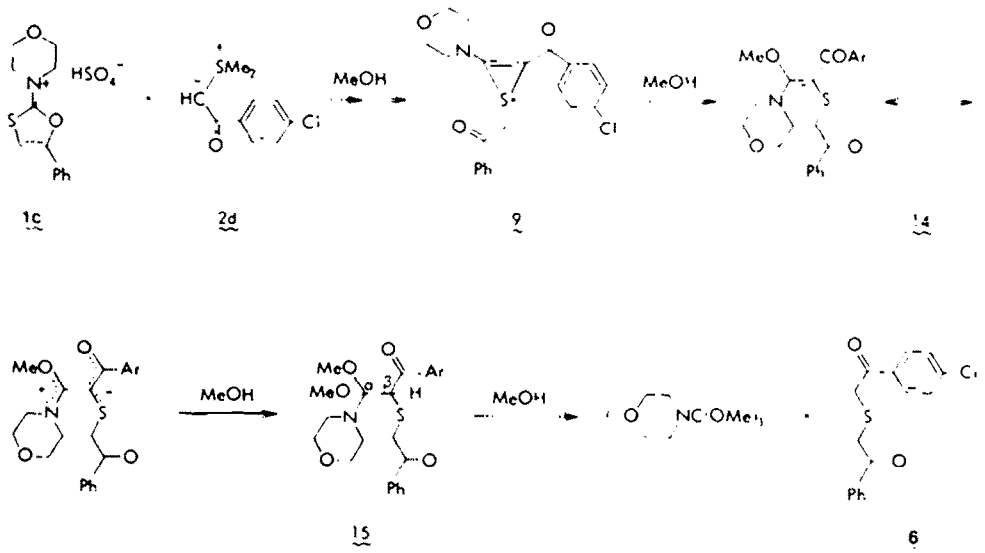

Fig. 4. Reaction course of **1** with **2** in MeOH.

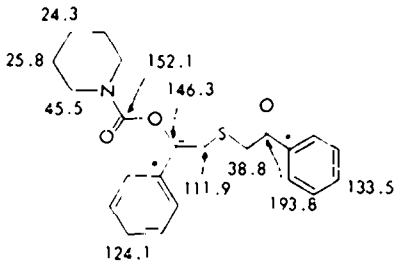

Chart 7.

and 135.11 ppm, and other eight aromatic carbons collapse into near 128 ppm. (Found: C, 69.07; H, 6.33; N, 3.77; S, 8.71. Calc. for $C_{22}H_{21}NO_3S$: C, 69.26; H, 6.08; N, 3.67; S, 8.41%).

Reaction of **1a** *with* **2b**. A mixture of 1.37 g of **1a** and 1.94 g of methylphenylsulphonium phenacylide **2b** in 40 ml of CH_2Cl_2 was stirred for 6 h at room temp. The mixture became a red solution. Excess water was added and the mixture was shaken rigorously. The organic layer was separated, dried and concentrated. The residue was washed with ether. Recrystallization from AcOEt afforded **3a** (0.94 g, 62%), which was identified by spectral comparison with the above product **3a**.

Reaction of **1a** *with* **2c**. The reaction was the same as the above. The product **3b** was obtained in 58% yield after recrystallization from AcOEt: m.p. 97–100°; NMR ($CDCl_3$) δ 8.30–7.95 (q, 4H, *p*-NO_2Ph), 7.27 (s, 5H, Ph), 6.33 (s, 1H, methine), 4.08 (s, 2H, CH_2), 3.70–3.14 (m, 4H, piperidino), 1.90–1.35 (m, 6H, piperidino); mass spectrum *m/e* (calc.), sample heater temp., 140°, 84.0803 (84.0811, $C_5H_{10}N$), 105.0344 (105.0372, PhCO), 112.0798 (112.0762, $C_5H_{10}NCO$), 134.0167 (134.0189, C_8H_6S), 178.0079 (178.0088, $C_9H_6O_2S$, 12), 188.1065 (188.1074, $C_{12}H_{14}NO$), sample heater temp., 165°, 112.0768 (112.0762, $C_5H_{10}NCO$), 150.0181 (150.0190, $O_2NC_6H_4CO$), 230.1186 (230.1180, $C_{14}H_{16}NO_2$, 13), 297.0449 (297.0458, $C_{16}H_{11}NO_3S$). (Found: C, 61.44; H, 5.35; N, 6.59; S, 7.62. Calc. for $C_{22}H_{22}N_2O_5S$: C, 61.95; H, 5.20; N, 6.57; S, 7.52%).

Reaction of **1b** *with* **2c**. A mixture of 0.90 g of **1b** and 1.80 g of **2c** in 15 ml of CH_2Cl_2 was stirred for 2 h with external cooling. The mixture turned yellow, then a precipitate formed. Excess water was added, and the organic layer was separated, dried and concentrated. Recrystallization from AcOEt gave 0.65 g (71%) of **3c**: m.p. 137–138°; NMR ($CDCl_3$) δ 8.30–7.77 (q, 4H, *p*-NO_2Ph), 7.27 (s, 5H, Ph), 7.11 (s, 5H, Ph), 3.73 (s, 2H, CH_2), 3.51 (broad s, 8H, morpholino). (Found: C, 63.62; H, 4.69; N, 5.97. Calc. for $C_{27}H_{24}N_2O_6S \cdot \frac{1}{2}H_2O$: C, 63.52; H, 4.82; N, 5.49%).

Hydrazone formation of **3a**. A solution of 0.267 g of **3a** and 0.378 g of phenylhydrazine in 10 ml of CH_2Cl_2 was stirred for 2 h at room temperature. The mixture was separated by filtration and the filtrate was washed with water, separated and dried. Evaporation of the solvent followed by washing with ether gave a crude product. Recrystallization from acetone gave 0.190 g of hydrazone **4**: m.p. 154–155°; NMR ($CDCl_3$) δ 8.63 (broad s, 1H, NH), 8.00–7.03 (m, 15H, Ph), 6.37 (s, 1H, methine), 4.02 (s, 2H, CH_2), 3.58 and 1.61 (broad s, 4H and 6H, respectively, piperidino); IR (KBr, cm^{-1}) 3260 (ν_{N-H}), 1693 ($\nu_{C=O}$, urethane), 1602 ($\nu_{C=C}$ and $\nu_{C=N}$); UV (EtOH) λ_{max} nm (log ϵ), 232 (4.46), 248 (4.31), 295 (4.41), 342 (4.29). (Found: C, 71.60; H, 6.22; N, 9.42; S, 7.06. Calc. for $C_{28}H_{29}N_3O_2S$: C, 71.31; H, 6.20; N, 8.91; S, 6.80%).

Reaction of **1c** *with* **2a** *in acetonitrile at low temperature*. A mixture of 1.20 g of **1c** and 1.30 g of **2a** in 20 ml of MeCN was stirred at −20° for 4 h. The temp. during the reaction was allowed to reach 10°. The mixture was separated by filtration to give a colourless product **5a**, 1.80 g (98% as **5a** hydrogen sulphate). However, this was unstable and decomposed into a tarry substance on exposure to air. When **5a** was dissolved in d_6-DMSO, the solution turned yellow: NMR δ 8.22–7.30 (m, 10H, Ph), 4.00–3.40 (broad s, 8H, morpholino), 3.12 (s, 6H, SMe_2), methylene protons might be included in the region of water near δ 4.94 (broad).

Conversion of intermediate to **3d**. The hygroscopic intermediate **5a** (1.70 g) was dissolved in 10 ml of water, and the solution was stirred for 10 min at room temperature. The mixture was extracted with $CHCl_3$, separated, dried and concentrated. Recrystallization from AcOEt gave 750 mg (60%) of **3d**: m.p. 132–134°; NMR ($CDCl_3$) δ 8.10–7.83 (m, 2H, Ph), 7.63–7.13 (m, 8H, Ph), 6.47 (s, 1H, methine), 4.08 (s, 2H, CH_2), 3.67 (broad s, 8H, morpholino). (Found: C, 65.69; H, 5.74; N, 3.35; S, 8.46. Calc. for $C_{21}H_{21}NO_4S$: C, 65.78; H, 5.52; N, 3.65; S, 8.36%).

Attempted isolation of **5b**. A mixture of 1.00 g of **1a** and 1.10 g of **2a** in 10 ml of MeCN was stirred for 1 h at room temp. The mixture became a yellow-orange suspension. The mixture was separated by filtration and the filtrate was concentrated *in vacuo*. The residue was dissolved in 5 ml of MeCN and addition of excess ether gave a yellow product (**5b** hydrogen sulphate), which was highly hygroscopic on exposure to air. It was dissolved in 5 ml of MeCN, then 2.0 ml of 60% $HClO_4$ aq was added. Addition of excess ether followed by separation by filtration gave 350 mg (19%) of **5b**: dec. 125–127°, NMR (d_6-DMSO) δ 8.13–7.30 (m, 19H, Ph), 5.47 (s, 2H, CH_2), 4.27–3.57 (m, 4H, piperidino), 3.05 (s, 6H, SMe_2), 1.90–1.73 (m, 6H, piperidino); IR (KBr, cm^{-1}) 1680 ($\nu_{C=O}$), 1655 ($\nu_{C=O}$, conjugated), 1085 (ClO_4^-). (Found: C, 46.21; H, 4.75; N, 2.41; S, 10.42; Cl, 11.72. Calc. for $C_{28}H_{29}Cl_2NO_{10}S_2$: C, 46.01; H, 4.67; N, 2.24; S, 10.23; Cl, 11.32%).

Reaction of **11** *with* **2a**. A mixture of 0.450 g of **11** (perchlorate) and 0.80 g of **2a** in 10 ml of CH_2Cl_2 was stirred for 1 h at room temperature. The mixture was filtered. Excess ether was added to the filtrate and the precipitate was collected by filtration. Recrystallization from AcOEt gave 400 mg of **8a** (41%): dec. 134–135°; NMR (d_6-DMSO) δ 7.57–7.10 (m, 9H, ph), 6.65 (s, 1H, methine), 6.28 (s, 1H, methine), 3.10 (s, 6H, SMe_2). (Found: C, 50.08; H, 4.03; S, 20.95. Calc. for $C_{16}H_{17}BrOS_3 \cdot H_2O$: C, 50.11; H, 4.20; S, 21.12%).

Reaction of **1c** *with* **2d** *in methanol*. A mixture of 0.90 g of **1c** and 1.25 g of **2d** in 20 ml of MeOH was stirred for 2 h at room temp. Excess ether was added and the precipitate was removed by filtration. The filtrate was concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel with ether as the eluant. A fraction of $R_f = 0.85$ was collected. Recrystallization from EtOH yielded 250 mg (32%) of **6**: m.p. 80–81°; NMR ($CDCl_3$) δ 8.03–7.18 (m, 9H, Ph), 3.95 (s, 2H, CH_2), 3.92 (s, 2H, CH_2). (Found: C, 63.00; H, 4.36; Cl, 11.90; S, 10.78. Calc. for $C_{16}H_{13}ClO_2S$: C, 63.05; H, 4.30; Cl, 11.63; S, 10.52%).

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