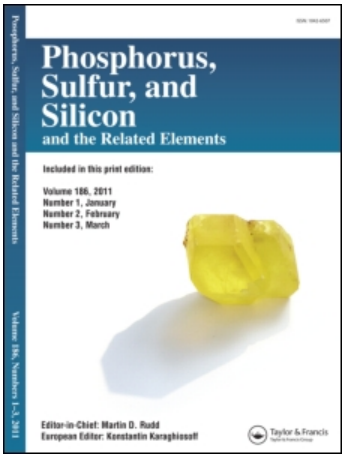

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STUDY OF THE ESCHENMOSER SULFIDE CONTRACTION METHOD WITH AND WITHOUT A THIOPHILE

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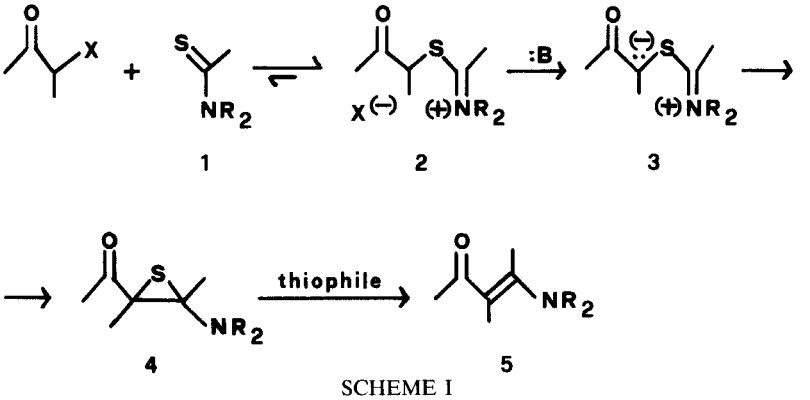
Results obtained and observations made by applying the title method for the synthesis of enaminones **5a–o**, using triphenylphosphine as a thiophile and triethylamine as a base, are reported. The product distributions of the deprotonations of α-phenacylthio iminium bromides with and without thiophile and those known from thiouronium and heterocyclic thionium analogs are compared.

Key words: Enaminones; α-phenacylthio iminium bromides; disulfides; thiiranes.

N,N-Disubstituted enaminones are useful intermediates[1] which can be prepared through a variety of procedures including reactions of secondary amines with β-diketones,[2] oxymethylene,[3] β-dialkoxy,[4] β-chlorovinyl,[5] β-alkylthioalkenyl,[6] β-alkylsulfinyl alkenyl[6] and β-cyanovinyl[7] ketones, reactions of ketones and secondary amines with N,N-dimethylformamide acetals[8] and orthoesters,[9] reactions of enamines with ketenes[10] and acid chlorides,[11] additions of amines to acetylenic ketones,[12] palladium assisted aminations of olefines[13] and palladium induced dehydrogenations of β-amino ketones.[14]

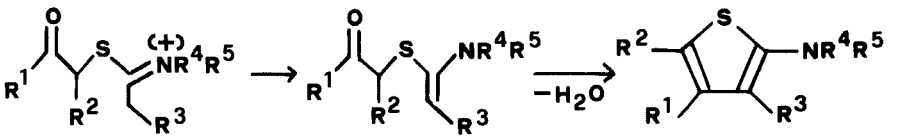
Another procedure which proved also viable is the Eschenmoser sulfide contraction method[15] based on the deprotonation of α-thioiminium halides accessible by alkylation of tertiary thioamides with active α-halogeno ketones. In the last decade this method has been widely applied for the synthesis of enamino esters as precursors of keto esters,[16] natural products,[17] alkaloids,[18] heterocyclic structures[19] and macrocyclic β-keto lactones.[20] To obtain satisfactory yields, however, the method requires a phosphorous thiophilic reagent. Bis(3-dimethylaminopropyl)phenylphosphine[15] developed by the same Eschenmoser works very well serving the dual role of base to abstract the α-proton to the carbonyl group and of thiophile to assist the sulfur estrusion; bis(3-morpholinylpropyl)phenylphosphine[16] developed by Rapoport appears to be equally effective. Generally yields higher than 80% are not achievable because of the reversibility of the thioamide alkylation reaction. In some syntheses of enamino esters the back-reaction was curtailed or eliminated by exchanging the halogen anion for a less nucleophilic anion such as a triflate and by using solvents such as dichloro- and trichloromethane.[16]

In the absence of the desulfurating reagent yields are rather low (<12%).[21] The phosphorous thiophile is assumed to assist the desulfurization of the unisolable intermediate thiirane **4** produced from the 4 π-electrocyclic closure of the thiocarbonyl ylid **3**, initially formed from the deprotonation of the α-thioiminium ion **2**[15] (Scheme I).



SCHEME I

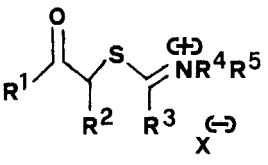
A limitation of the method consists in the competitive production of thiophenes **6** occurring according to Scheme II, when the thioamide α-protons are enough acid to be abstracted in preference to the carbonyl α-protons.[20–22]



SCHEME II

Following the Eschenmoser method, based on triphenylphosphine as a thiophile and triethylamine as a base, we could prepare enamino ketones **5a–o** from bromides **2a–o**, but not **5p,q** from **2p,q** and **5r,s** for the not accessibility to **2r,s**. Structures **5a–s** were required to obtain the corresponding enaminothiones planned to study their cycloaddition reactions with electrophilic ethylenes and acetylenes.[8]

Compd.s	R^1	R^2	R^3	R^4	R^5
2, 5a	Bu^t	H	H	Me	Me
2, 5b	Ph	H	H	Me	Me
2, 5c	Naf	H	H	Me	Me
2, 5d	Ph	H	Me	Me	Me
2, 5e	Ph	H	Me	Pyr	
2, 5f	Ph	H	Me	Pip	
2, 5g	Ph	H	Me	Mor	
2, 5h	Ph	H	Ph	Me	Me
2, 5i	Ph	H	Ph	Pyr	
2, 5l	Ph	H	Ph	Pip	
2, 5m	Ph	H	Ph	Mor	
2, 5n	Ph	Me	H	Me	Me
2, 5o	Ph	Ph	H	Me	Me
2, 5p	Ph	Me	Me	Me	Me
2, 5q	Ph	Ph	Me	Me	Me
2, 5r	Ph	Me	Ph	Me	Me
2, 5s	Ph	Ph	Ph	Me	Me



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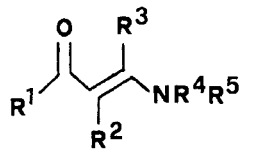


5

Me=methyl, Bu^t=butyl, Naf=naftyl, Ph=phenyl, Pyr= pyrrolidino, Pip= piperidino, Mor= morpholino

Prompted by the interest of some of us into the chemistry of conjugated thiocarbonyl ylides,[23–25] parallely we analyzed the product distributions of the deprotonations of some α-phenacylthio iminium bromides, carried out in the absence of the desulfurating reagent, in order to obtain information on the behavior of thiocarbonyl ylides directly conjugated with a C=O double bond. While the deprotonations of *S*-phenacyl thiouronium[26] and heterocyclic thionum[27,28] salts have been studied in detail, that one of thioamidium analogs has received attention only in relation to the preparation of enamino ketones which result in minor products.[21]

While the syntheses and cycloaddition reactions of the planned enaminothiones will be the subject of a later report, herein we wish to report the observations made in the preparations of the starting α-thioiminium salts **2a–s** required for enaminones **5a–s** and the results obtained by applying the episulfide contraction procedure to the synthesis of terms **5a–o** and **5b,d,g,h,m** in the presence and in the absence of triphenylphosphine, respectively.

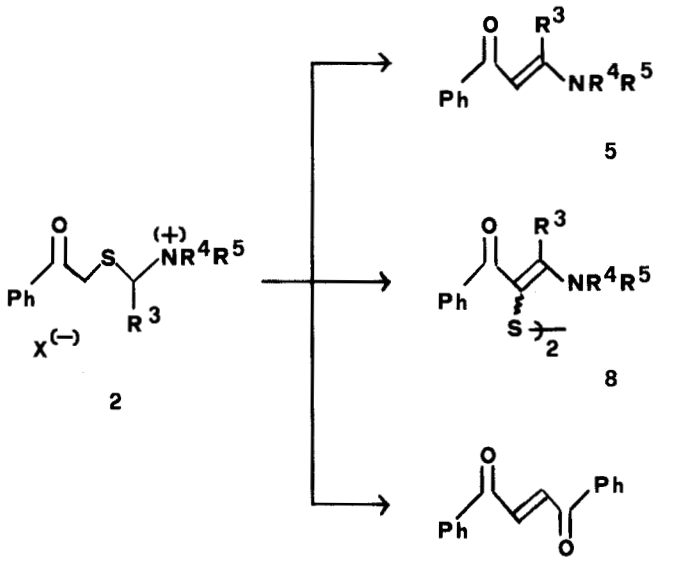
RESULTS AND DISCUSSION

α-Thioiminium bromides **2a–m**, were easily obtained by allowing the requisite primary α-bromoketones and thioamides in concentrated solutions of dry dichloromethane under stirring for 12 hours at room temperature. This procedure proved to afford the highest yields (>90%) among those attempted: in molten state, in solutions of different solvents at room and reflux temperature.

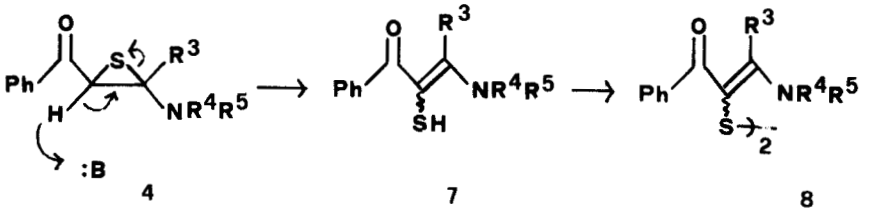
Following the above procedure N,N-dimethyl thioformamide and thioacetamide afforded moderate yields (50–60%) of bromides **2n,p** with 2-bromopropiophenone, and lower yields (30–40%) of **2o,q** with desyl bromide. Starting from N,N-dimethyl thiobenzamide the preparation of bromides **2r,s** could not be accomplished. Forcing conditions, as well as utilizing the corresponding iodides or triflates as more effective alkylating reagents, were of no avail. For the purification of the obtained salts it usually sufficed if they were thoroughly washed with benzene. On the other hand upon recrystallization from hot solvents, they suffer extensive decomposition to the reactants. Their purity and identification was checked by NMR and IR spectroscopy. In the NMR spectra of thioformamidium and thioacetamidium bromide methylenic and methinic protons appear down-shifted of 0.8–1.0 ppm relative to those of starting bromoketones, and those of thiobenzamidinium bromides of 0.3–0.4 ppm; thioformyl protons of **2a–c,n,o** fall in the range 11.20–11.80 δ. For all bromides an open structure was indicated by a intense absorption band at 1680 cm^{-1} in their IR spectra.

The treatment of a suspension of α-thioiminium bromides **2a–m** in chloroform containing 1.2 equivalents of triphenylphosphine (triethylphosphite proved to work also well giving the same results) with a slight excess (1.2 equivalents) of triethylamine at room temperature under a blanket of nitrogen gave satisfactory yields (61–78%) of enaminones **5a,m,** but lower yields (38, 42%) of **5n,o** were isolated from bromides **2n,o**. No significant amounts of enaminones **5p,q** could be obtained from **2p,q**, but 2-dimethylamino-4,5-diphenylthiophene **6** was isolated as a major reaction product from the deprotonation of **2q**.

The obtained enaminones **5a–n** were separated from the other components of the reaction mixture, free from the insoluble material in ether, by flash-chroma-



SCHEME III

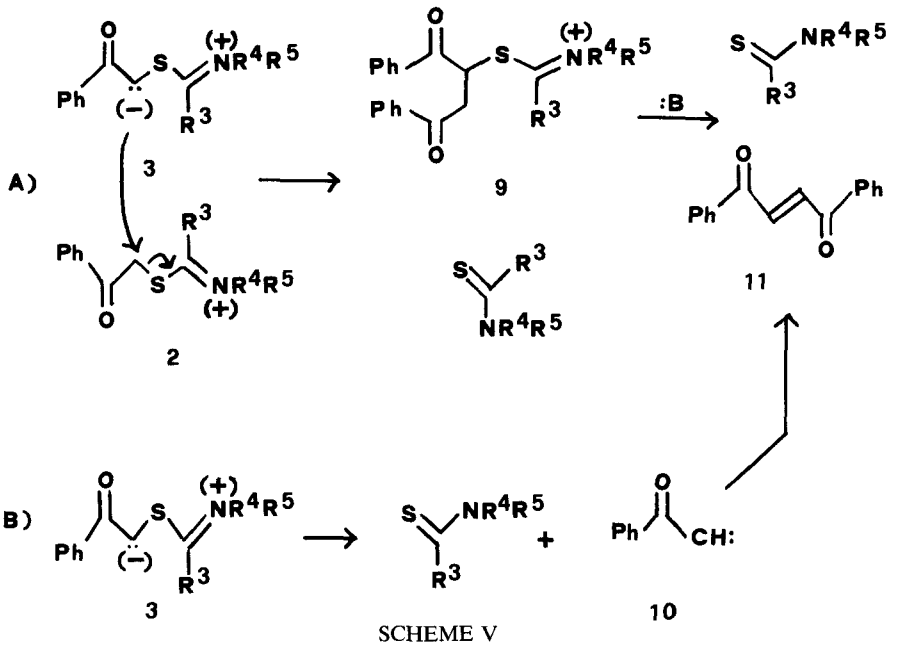


SCHEME IV

tography conducted by using as eluent a 2:8 mixture of ethyl acetate-cyclohexane containing 1% triethylamine, which proved to prevent the enaminone hydrolysis. Starting thioamides and triphenylphosphine sulfide were isolated as secondary more abundant products.

The structural elucidation of all isolated compounds was performed by spectroscopic methods and was supported for the cases of known derivatives by comparison of their physical and spectral data with those of literature and/or authentic samples. As in the other preparation methods enaminones **5a–c** were obtained as pure *E*-isomers as inferred by the large coupling constants (12–13 Hz) of the two doublets relative to the two vinylic protons. The most β-substituted enaminones were isolated as mixtures of the two geometrical isomers. Their ^{1}H NMR spectra were characterized by two close singlets in the range 5.26–6.05 δ for the vinylic proton. The carbonyl stretching absorption bands fall between 1630 and 1640 cm^{-1} in line with literature values found for enaminones.[29]

To study the reaction course of α-thioiminium salt deprotonations in the absence of thiophile, α-phenacylthio derivatives **2b,d,g,h,m** were chosen. They were subjected to the same deprotonation conditions above described, but without triphenylphosphine. Enaminones **5b,d,g,h,m** were isolated in low yields (20–25%)



SCHEME V

along with starting thioamides (~30%), disulfides **8a–e** (10–15%) and smaller amounts (~5%) of trans-dibenzoylethene **11** (Scheme III). This latter was identified by comparison of its spectral data with those of an authentic sample. The structures of disulfides **8** were based on their spectral data and smooth conversion into the corresponding enaminones by desulfurating hydrogenolysis with Raney nickel.[30] Disulfides **8** clearly derive from the spontaneous oxidation of intermediate enethiols **7** generated by thiirane isomerization, which competes with sulfur estrusion in the absence of thiophile (Scheme IV). The isomerization is induced by the base as shown by the fact that by using a large excess (5 equivalents) of triethylamine in the deprotonation of **2b**, disulfide **8a** becomes the most abundant product.

For the formation of the dibenzoylethene **11** the two mechanisms proposed for the olefine formation from thiocarbonyl[26] and sulfonium[31] ylides can be invoked. The α-thioiminium cation **2** could undergo a replacement of thioamide moiety upon attack of the nucleophilic center of the transient thiocarbonyl ylid **3** to give a new cation **9**, which then undergoes a base induced β-elimination to afford ethene **11**. To the production of **11**, however, a contribute of phenacyl bromide deriving from the back-reaction of **2**, cannot be ruled out since it can also undergo a nucleophilic substitution to give the same cation **9** (Scheme V, path A). Alternatively the ylid **3** could dissociate into thioamide and carbene **10**, which latter then dimerizes (Scheme V, path B).

The application of the sulfide contraction method to accessible α-thioiminium salts **2a–m** affords satisfactory yields of enaminones **5a–m** under our conditions. These are obtained as single *E*-stereoisomers in the cases of non sterically demanding derivatives **5a–c**, but as mixtures of the two geometrical isomers in the most β-substituted derivatives **5d–m**. The introduction of an α-substituent (an even not bulky methyl or a phenyl) into the alkylating reagent reduces the formation

of α-thioiminium salts **2n–q** and inhibits that of **2r,s**. Upon deprotonation, only **2n,o** afford low yields of corresponding enaminones **5n,o**. Therefore, the Eschemoser method becomes not convenient or not practicable for α,β-disubstituted enaminones. The failure of the enaminone formation from **2p–q** can be ascribed to the congestion of the transition state leading to the intermediate thiirane **4**.

Besides starting thioamides and lower yields (20–25%) of enaminones, the deprotonation in the absence of desulfurating reagent affords disulfides **8** (10–15%) along with small amounts (~5%) of dibenzoylethene **11**. The formation of this latter was unexpected in the light of literature data concerning the deprotonations of the analogous *S*-phenacyl thiouronium[26] and heterocyclic thionium[27,28] salts, which give only the corresponding disulfides beside the phenacylidene derivatives. Symmetrically disubstituted ethylenes are reported to be formed from the decomposition of the thiocarbonyl ylides stabilized by a combination of electron-acceptor and -donor substituents.[26,32]

The absence of dibenzoylethene **11** among the products of the deprotonations performed in the presence of triphenylphosphine suggests that the phosphorous reagent plays a role other than that proposed,[15] and probably it interacts with the precursor of the intermediate thiirane, the starting α-thioiminium cation or the initially formed thiocarbonyl ylid. An analogous consideration was also made by Rapoport on the basis of the results obtained by applying the sulfide contraction procedure to thiolactams alkylated with methyl bromoacetate.[17]

In agreement with the anticipations based on the instability of a 2-amino-1,3-oxathiolene structure, no products deriving from a 6π-electrocyclic closure of transient thiocarbonyl ylides were observed. A spiro-1,3-oxathiolene derivative was reported to be formed from 2-(*p*-bromophenacylthio)-1,3-dithiolanium bromide,[27] but later its formation was not confirmed.[28]

Finally, the formation of **6**, but not of **5q**, from **2q** suggests that the limitation of the Eschenmoser method concerning the competitive formation of thiophene nuclei shows also for α-thioiminium salts containing α-protons to the thioamide moiety less acid than α-protons to the carbonyl group when steric interactions of substituents in the initially formed thiocarbonyl ylides prevent the formation of thiirane leading to enaminone.

EXPERIMENTAL

All melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker WP 80 spectrometer using tetramethyl silane as internal standard and deuteriochloroform solutions, unless otherwise stated. IR spectra (potassium bromide or nujol mulls) were taken on a Perkin Elmer 281 spectrophotometer, and mass spectra on a VG ZAB-2SE spectrometer operating at 70 eV. Analytical TLC was conducted on Merck silica gel 60-F_{254} pre-coated aluminium plates. Separations of reaction crudes were performed by flash and centrifugally enhanced preparative thin layer (CTLC) chromatography using Merck silica gel 60 and 60-PF_{254}, respectively. Cyclohexane containing 1% triethylamine with increasing proportions of ethyl acetate was used as eluent, unless otherwise stated.

Starting materials. N,N-dimethylamino thioformamide, dibenzoylethene, all α-bromoketones and anhydrous solvents were purchased from Aldrich Chemical Co. The other thioamides were obtained following literature methods.[33–35] 1-Phenyl- and 1-methyl-1-benzoyltrifluoromethanesulfonate were prepared following the Vedejs procedure[36] and were used in the crude state without purification in order to avoid their partial decomposition during isolation.

General procedure for the preparations of α-thioiminium bromides **2**. A solution of the requisite thioamide **1** (20 mmol) and α-bromoketone (24 mmol) in dry dichloromethane (30 ml) was allowed under stirring and an atmosphere of nitrogen at room temperature in the dark for 12 hours. Solvent was then removed under reduced pressure and at room temperature to give a solid or a viscous oil which solidified after standing over anhydrous diethyl ether for several hours at 0°C. The solid was washed with anhydrous benzene (four 10 ml portions) and then dried under "vacuum". This procedure proved to afford the highest yields among those attempted: in molten state, in solution of other solvents (acetonitrile, tetrahydrofuran, acetone, diethyl ether, benzene) at room and reflux temperature. Bromides **2a–m** were obtained in excellent yields (>90%), but modest yields (50–60%) of bromides **2n,p** and much lower yields (30–40%) of bromides **2o,q** were obtained from N,N-dimethyl thioformamide and thioacetamide with 2-bromopropiophenone and 2-bromo-2-phenylacetophenone, respectively. Starting from the two latter bromides and N,N-dimethyl thiobenzamide no preparations of **2r,s** could be accomplished. Forcing conditions by working at the temperature of refluxing solvent or in dry acetonitrile in the presence of sodium iodide (25 mmol) were of no avail. An attempt to obtain the corresponding triflates by treating N,N-dimethyl thiobenzamide with 1-methyl- and 1-phenyl-1-benzoyl-methane trifluorosulfonate had no success.

The obtained bromides **2a–q** were not further purified after washings with benzene, because they suffered extensive decomposition to the reactants on attempted recrystallization from hot solvent. Their purity and identification was checked by NMR and IR spectroscopy. In the NMR spectra of **2a–c,n,o** thioformyl protons fall in the range 11.20–11.80 δ; methylenic and methinic protons of thioformamidium and thioacetamidium bromides appear down-shifted of 0.8–1.0 ppm relative to those of starting bromoketones, while those of thiobenzamidium bromides of 0.3–0.4 ppm. IR spectra show an intense absorption band at 1680 cm^{-1} for the carbonyl stretching.

Triethylamine induced deprotonation of α-thioiminium bromides **2a–q** *in the presence of triphenylphosphine. General procedure for the preparation of enaminones* **5a–o**. To a stirred suspension of α-thioiminium bromides **2a–q** (10 mmol) in dry dichloromethane (50 ml) containing triphenylphosphine (12 mmol) a solution of triethylamine (12 mmol) in the same solvent (20 ml) was added dropwise in a period of 5 minutes and stirring was kept 2 hours at room temperature under an atmosphere of nitrogen.

TABLE I

Yields and m.p.s of obtained enaminones **5a–o**

No.	Compounds[a] R^1	R^2	R^3	R^4	R^5	yield[b] (%)	M.p. (°C)	Molecular formula[c] or Lit. m.p. or b.p./mm (°C)
5a	Bu^t	H	H	Me	Me	72	oil[d]	oil[d,e]
5b	Ph	H	H	Me	Me	78	95-97	96[f]
5c	Naf	H	H	Me	Me	69	65-67	$C_{15}H_{15}NO$
5d	Ph	H	Me	Me	Me	67	67-69	69[g]
5e	Ph	H	Me	Pyr		62	164-165	165-166[h]
5f	Ph	H	Me	Pip		61	97-98	94-96[h]
5g	Ph	H	Me	Mor		64	139-142	141-142[h]
5h	Ph	H	Ph	Me	Me	74	108-109	$C_{17}H_{17}NO$
5i	Ph	H	Ph	Pyr		72	97-99	$C_{19}H_{19}NO$
5l	Ph	H	Ph	Pip		70	92-94	98-99[i]
5m	Ph	H	Ph	Mor		71	94-96	94-95[l]
5n	Ph	Me	H	Me	Me	42	oil	126/0.1 mm[m]
5o	Ph	Ph	H	Me	Me	38	130	128-129[m]

[a] Bu^t=t-butyl, Me=methyl, Ph=phenyl, Naf=naftyl, Pyr=pyrrolidino, Pip=piperidino, Mor=morpholino. [b] Yield of isolated product; purity checked by IR and NMR spectra. [c] Mass spectra and microanalyses were in satisfactory agreement with the calculated values (C, H, N, ±0.4%). [d] Oil solidifying on standing at r.t. [e] Ref 38. [f] Ref. 9. [g] Ref. 39. [h] Ref. 40. [i] Ref. 41. [l] Ref. 6. [m] Ref. 42.

TABLE II

Spectral data (IR and ^{1}H NMR) of enaminones **5a–o**

Compd. No.	IR (ν_{max},cm^{-1})	^{1}H NMR (δ,ppm)
5a	1640,1580,1540	1.31 (s, 9 H); 2.98 (s, 6 H); 5.27 (d, J=12.0 Hz, 1 H); 7.60 (d, J=12.0 Hz, 1 H)
5b	1640,1580,1540	2.96 (s, 6 H); 5.70 (d, J=12.4 Hz, 1 H); 7.17-7.28 (m, 3 H); 7.51 (d, J=12.4 Hz 1 H); 7.81-8.30 (m, 2 H)
5c	1638,1586,1540	2.95 (s, 6 H); 5.88 (d, J=13.5 Hz, 1 H); 7.17-7.37 (m, 5 H); 7.58-8.32 (m, 3 H)
5d	1635,1580,1540	2.47 (s, 3 H); 2.92 (s, 6 H); 5.67 and 5.80 (2s, total 1 H, 9.5:0.5); 7.16-7.28 (m, 3 H); 7.75-8.15 (m, 2 H)
5e	1635,1586,1542	1.92 (m, 4 H); 2.40 (s, 3 H); 3.30 (m, 4 H); 5.26 (s, 1 H); 7.06-7.39 (m, 3 H); 7.60-7.84 (m, 2 H)
5f	1640,1590,1540	1.37 (m, 6 H); 2.58 (s, 3 H); 3.31 (m, 4 H); 5.31 (s, 1 H); 7.20-7.41 (m, 3 H); 7.64-7.86 (m, 2 H)
5g	1635,1580,1530	2.40 (s, 3 H); 3.40 (m, 4 H); 3.83 (m, 4 H); 5.28 (s, 1 H); 7.28-7.45 (m, 3 H); 7.75-7.90 (m, 2 H)
5h	1640,1590,1535	2.85 and 2.99 (2s, total 6 H, 3:7); 5.79 and 5.87 (2s, total 1 H, 3:7); 7.10-7.44 (m, 8 H); 7.90-8.15 (m, 2 H)
5i	1640,1580,1538	1.33 (m, 4 H); 2.92 (m ,4 H); 5.78 and 5.86 (2s, total 1 H, 1:9); 7.19-7.25 (m, 8 H); 8.10-8.30 (m, 2 H)
5l	1636,1588,1525	1.25 and 1.31 (2m, total 6 H, 4:6); 2.83 and 3.16 (2m, total 4 H, 4:6); 5.78 and 5.92 (2s, total 1H, 4:6); 7.14-7.42 (m, 8 H); 8.03-5.19 (m, 2 H)
5m	1640,1600,1545	3.17-3.21 (m, 4 H); 3.56-3.87 (m, 4 H); 5.90 and 6.05 (2s, total 1 H, 2:8); 7.13-7.40 (m, 8 H); 7.57-7.90 (m, 2 H)
5n	1635,1590,1540	2.10 (s, 3 H); 2.98 (s, 6 H); 6.78 (s, 1 H); 7.50 (br s, 5 H)
5o	1620,1595.1548	2.90 (s, 6 H); 7.03-7.14 (m, 8 H); 7.05 (s, 1 H); 7.58-7.70 (m, 2 H)

The solvent was removed under reduced pressure and the resulting residue was triturated in anhydrous diethyl ether (30 ml). The insoluble material (triethylammonium and phenacyl triphenylphoshophonium bromide) was filtered off and the filtrate evaporated to obtain a residue which was subjected to flash chromatography. The following enaminones were isolated as compounds chromatographically pure (TLC, silica gel, cyclohexane-ethylacetate, 70:30): 2,2-dimethyl-5-dimethylamino-4-penten-3-one (**5a**), 1-phenyl- (**5b**), 1-naftyl-3-dimethylamino-2-propen-1-one (**5c**), 3-dimethylamino- (**5d**), 3-pyrrolidino- (**5e**), 3-piperidino- (**5f**), 3-morpholino-1-phenyl-2-buten-1-one (**5g**), 3-dimethylamino- (**5h**), 3-pyrrolidino- (**5i**), 3-piperidino- (**5l**), 3-morpholino-1,3-diphenyl-2-propen-1-one (**5m**), 1-phenyl-2-methyl- (**5n**) and 1,2-diphenyl-3-dimethylamino-2-propen-1-one (**5o**). Their yields, physical and spectral data are gathered in Tables I and II. Starting thioamides **1** and triphenylphosphine sulfide were also isolated as main secondary products. These latter were identified by mixed m.p.s and superimposable IR spectra.

From reaction mixtures of bromides **2p,q** corresponding enaminones **5p,q** could not be isolated. Only thiophene **6** was isolated in a 27% yield as the sole consistent reaction product from **2q**.

TABLE III

M.p.s, yields and spectral data of disulfides **8a–e**

No.	Compound[a] R[3]	R[4]	R[5]	M.p. (°C)	Yield[b] (%)	Molecular Formula	ν(CO) (cm^{-1})	δ($CDCl_3$) (ppm)
8a	H	Me	Me	122-26	14	$C_{22}H_{24}N_2O_2S_2$	1684	3.00 (br s, 12 H); 7.35 (br s, 10 H); 7.65 (s, 2 H)
8b	Me	Me	Me	56-60	12	$C_{24}H_{28}N_2O_2S_2$	1640	2.46 (s, 6 H); 2.96 (br s, 12 H), 7.05-7.60 (m, 8 H); 7.85-8.00 (m, 4 H)
8c	Me	Mor		61-65	10	$C_{28}H_{32}N_2O_4S_2$	1630	2.50 (s, 6 H); 3.15 (m, 8H); 3.55 (m, 8 H); 7.14-7.56 (m, 8 H); 7.68-7.75 (m, 4 H)
8d	Ph	Me	Me	86-90	15	$C_{34}H_{32}N_2O_2S_2$	1640	2.90 (s, 12 H); 7.17-7.41 (m, 16 H); 7.50-7.59 (m, 4 H)
8e	Ph	Mor		92-96	15	$C_{38}H_{36}N_2O_4S_2$	1630	3.08 (m, 8 H); 3.70 (m, 8 H); 7.42-7.67 (m, 16 H); 7.90-8.07 (m, 4 H)

[a]Me=methyl, Mor=morpholino, Ph=phenyl. [b]Yield of isolated product. [c]Mass spectra and microanalyses were in satisfactory agreement with the calculated values (C, H, N ±0.4%).

2-Dimethylamino-4,5-diphenylthiophene (6). m.p. 173-74°C; ν_{max} (KBr): 1600, 1556, 1510; δ ($CDCl_3$): 2.96 (s, 6H); 6.05 (s, 1H); 7.18 (br s, 5H); 7.23 (br s, 5H); m/z: 279 (M^+, 100), 202 (15), 191 (40), 121 (70), 88 (35), 77 (70).

Anal. Calcd. for $C_{18}H_{17}NS$: C, 77.38; H, 6.13; N, 5.01; S, 11.48.

Found: C, 77.45; H, 6.09; H, 4.90; S, 11.82.

Deprotonations of bromides **2b,d,h** conducted with triethylphosphite in lieu of triphenylphosphine gave the same results.

Triethylamine induced deprotonation of α-thioiminum bromides **2b,d,g,h,m** *in the absence of triphenylphosphine.* The above described procedure was followed, but without the triphenylphospine, with bromides **2b,d,g,h,m**. The residue obtained after remotion of triethylamine hydrobromide and ether evaporation, was subjected to CTLC. Elution gave in the order: trans-dibenzoylethene **11** (~5%), starting thioamides **1** (~30%), enaminones **5b,d,g,h,m** (20–25%) and finally disulfides **8**. The first compounds **1, 5** and **11** were identified by comparison of their IR spectra with those of authentic samples.

Di [1-benzoyl-2-dimethylaminoethenyl] disulfide (**8a**), its 2-methyl (**8b**) and 2-phenyl (**8c**) substituted derivatives, as well as the 2-morpholino analogs **8d,e** of **8b,c** showed not clean melting points indicating their existence as a mixture of geometrical isomers which were not separated. Their m.p.s., yields and spectral data are reported in Table III.

When the deprotonation of **2b** was performed by using a large excess (5 equivalents) of triethylamine, the yield of **8a** raised up to 50% and that of **5b** lowered to 8%.

Desulfurization of disulfides **8**. To a stirred solution of **8** (1 mmol) in ethanol (20 ml) Raney-nickel (W-2)[37] (6.5 g) was added at room temperature and stirring was kept for 2 hours. Filtration of the catalyst followed by evaporation of the solvent gave a residue from which corresponding enaminones **5** (~60%), identical with authentic samples, were isolated by CTLC.

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