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Thiocarbonyl Ylides. Attempted Preparation and Related Reactions[1)]

Shuichi Mitamura, Masaaki Takaku, and Hitosi Nozaki*
Department of Industrial Chemistry, Kyôto University, Yoshida, Sakyô-ku, Kyôto 606

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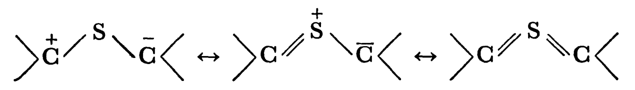
The attempted preparation of thiocarbonyl ylides (I) by the proton abstraction of thiouronium salts (III) has disclosed a fast isomerization of I to enethiols (V) (Y=H) and an alternative desulfurization to enediamines (VII) (Y=Ph), the by-products being olefins (VIII) and sulfides (IX). The second route to I examined consists of the reaction of tetramethylthiourea (II) with diazomalonate, which gives rise to enediamine (VII_g). Rotation about the C=C bond of enediamines is discussed on the basis of IR and NMR spectra.

Thiocarbonyl ylides should be resonance hybrides involving 1,3-dipole[2)] and tetravalent sulfur.

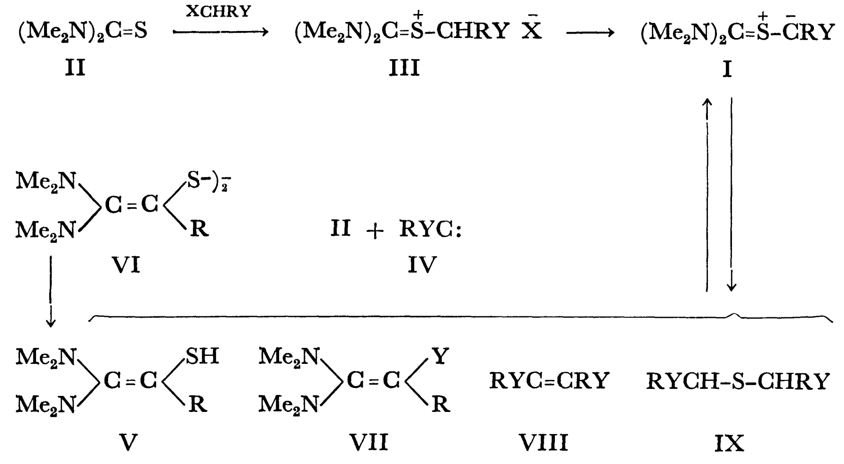


Recently Kellogg[3)] reported that the thermally-induced loss of nitrogen from 1,3,4-thiadiazolines afforded transient thiocarbonyl ylides, which then cyclized to thiiranes or alternatively reacted with azo compounds to give $[4_s+2_s]$ cycloadducts. Middleton[4)] isolated a stable thiocarbonyl ylide in the reaction of thiourea with dicyanocarbene.

The present authors attempted to obtain thiocarbonyl ylides (I) based on tetramethylthiourea (II) by the deprotonation of the corresponding thiouronium salts (III) and by the reaction of II with carbene IV (Scheme 1). These reactions failed to give the expected ylides (I), but, instead, they afforded four products: enethiols (V),[5)] enediamines (VII), olefins (VIII), and sulfides (IX) in the yields listed in Table 1.

Novel thiouronium salts (IIIa—IIIf) were readily prepared in good yields from II and halides, XCHRY (X=halogen: R=H or Ph: Y=COOEt, COOMe, COPh, Ph). The results of analyses are listed in Table 2, while the yields, the melting points, and the IR and NMR spectra are shown in Table 3.

Base Treatment of Thiouronium Salts (III). The



Scheme 1.

Table 1. Treatment of III with bases. Conditions and product distributions

Compd.	R	Y	X	Base	Solvent	Reaction time hr	Products (%) VI[a)]	VII	VIII	IX	II	Others
IIIa	COOEt	H	Br	Et_3N	THF	316	5.5	—	—	34	29	—
				NaH	THF	3	83	—	—	—	tr.	—
IIb	COOMe	H	Br	NaH	THF	3	41	—	—	—	7.4	—
IIIc	COPh	H	Br	Et_3N	THF	24	—	—	—	28	48	—
				NaH	DMSO	0.5	64	—	—	—	tr.	—
IIId	COOEt	Ph	Br	NaH	THF	24	c)	44	b)	—	42	d)
IIIe	COOMe	Ph	Br	NaH	THF	120	c)	31	12	—	34	—
IIIf	Ph	H	I	NaH	THF	120	—	—	—	23	8.5	—

a) Thiols V were isolated as the corresponding disulfides VI. b) There was obtained an oil whose IR suggested an olefinic ester structure. c) No thiol is expected. d) Elemental sulfur was obtained in 22% yield.

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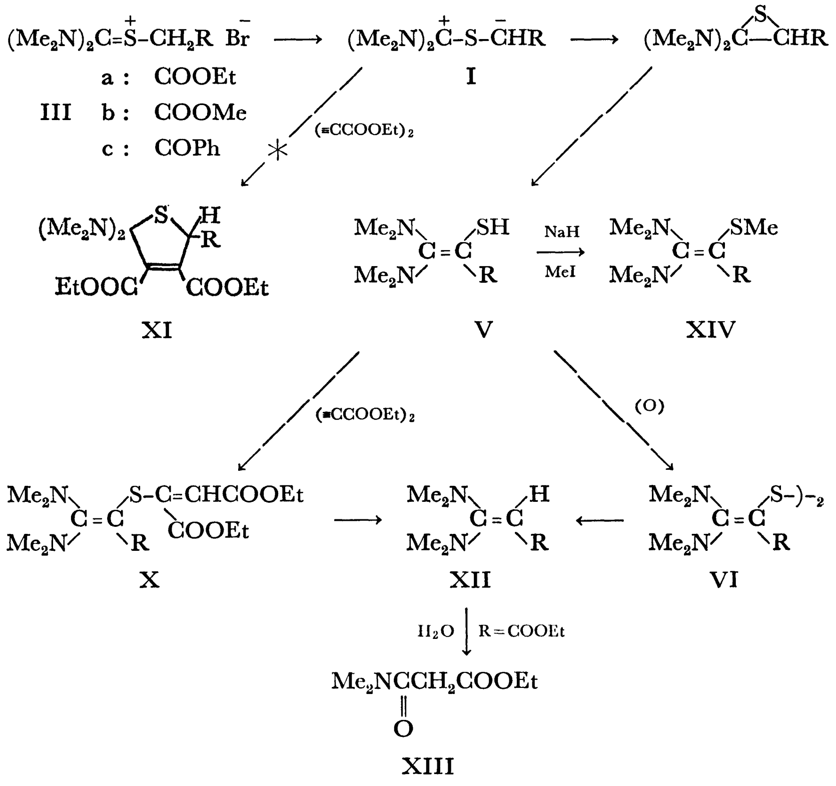
* To whom reprint requests should be addressed.

Table 2. Elemental analyses of thiouronium salts III

Compd.	R	Y	X	Formula	Calcd C	Calcd H	Found C	Found H
IIIa	COOEt	H	Br	$C_9H_{19}BrN_2O_2S$	36.1	6.4	36.2	6.5
IIIb	COOMe	H	Br	$C_8H_{17}BrN_2O_2S$	33.7	6.0	33.4	6.2
IIIc	COPh	H	Br	$C_{13}H_{19}BrN_2OS$	47.1	5.8	46.6	5.6
IIId	COOEt	Ph	Br	$C_{15}H_{23}BrN_2O_2S$	48.0	6.2	48.0	6.0
IIIe	COOMe	Ph	Br	$C_{14}H_{21}BrN_2O_2S$	46.5	5.9	46.6	6.0
IIIf	Ph	H	I	$C_{12}H_{19}IN_2S$	41.2	5.5	41.1	5.5

Table 3. Yields, melting points and spectral data of III

Compd.	Yield %	Mp °C	IR (KBr) cm^{-1}	NMR ($CDCl_3$) δ ppm
IIIa	83	131	1733, 1610	1.31(t, 3H), 3.54(s, 12H), 4.05(s, 2H), 4.23(q, 2H)
IIIb	84	117	1735, 1612	3.48(s, 12H), 3.77(s, 3H), 4.08(s, 2H)
IIIc	96	117	1683, 1602	3.44(s, 12H), 5.09(s, 2H), 7.4—8.3(m, 5H)
IIId	87	146	1722, 1604	1.21(t, 3H), 3.51(s, 12H), 4.23(q, 2H), 5.44(s, 1H), 7.3—7.6(m, 5H)
IIIe	99	137	1730, 1610	3.50(s, 12H), 3.80(s, 3H), 5.49(s, 1H), 7.3—7.5(m, 5H)
IIIf	96	151	1601, 703	3.41(s, 12H), 4.43(s, 2H), 7.2—7.5(m, 5H)



Scheme 2.

deprotonation of III may result in the formation of transient ylides (I). However, they do experience a fast isomerization to enethiols (V), which also are labile compounds; various products arising therefrom have been isolated to prove the intermediacy of these species.

A mixture of IIIa and excess diethyl acetylenedicarboxylate in tetrahydrofuran (THF) was treated with triethylamine to afford an adduct (Xa) in a 73% yield (Scheme 2). Similarly, IIIb gave Xb in a 70% yield. The isomeric structures, XIa and XIb, were excluded as follows. The mass spectra (Fig. 1) exhibited four fragment peaks due to carbon-sulfur bond fission. The desulfurization of Xa with Raney nickel afforded diethyl succinate and ethyl 3,3-bis(dimethylamino)acrylate (XIIa), whereas that of Xb gave diethyl succinate

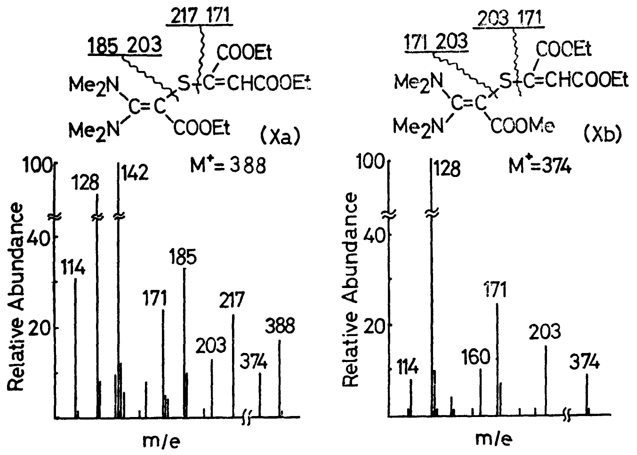


Fig. 1. Mass spectra of Xa and Xb.

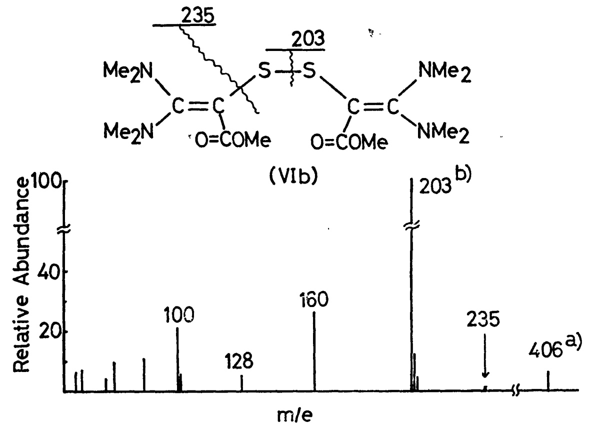


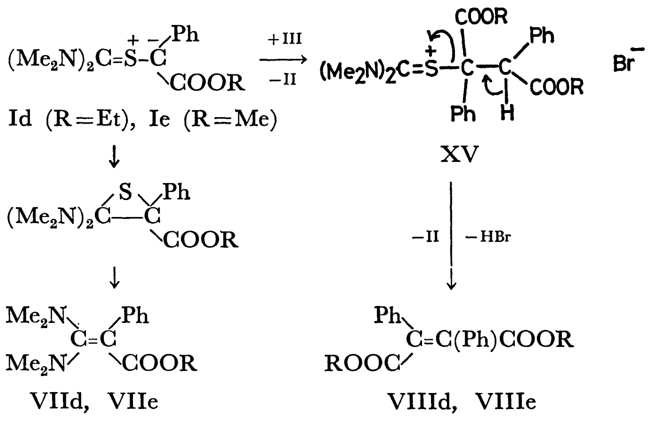
Fig. 2. High resolution mass spectrum of VIb.
a) Exact mass: 406.171, Calcd for $C_{16}H_{30}N_4O_4S_2$: 406.171. b) Exact mass: 203.086, Calcd for $C_8H_{15}N_2O_2S$: 203.085.

and XIIb. The hydrolysis of XIIa yielded ethyl *N*,*N*-dimethylmalonamidate (XIII), which was alternatively prepared from ethyl chloroformylacetate and dimethylamine.

The treatment of IIIa with equimolar sodium hydride in THF or dimethyl sulfoxide (DMSO), followed by a work-up, afforded VIa, which is the oxidative dimer of Va. Similarly, that of IIIb gave VIb. The spectral data, including the high-resolution mass spectrum of VIb (Fig. 2), were consistent with the structure. The desulfurization of VIa gave XIIa, and that of VIb yielded XIIb. When a solution of IIIa in carefully degassed THF was treated with 2 mol of sodium hydride and then with methyl iodide, there obtained a methylthio compound (XIVa) along with VIa. Applying a similar procedure to IIIb in dimethylformamide (DMF) gave XIVb.

The treatment of IIIc with sodium hydride in DMSO yielded VIc, whereas sulfide (IXc) was the predominant product in THF (Scheme 1, Table 1). DMSO seems to play the role of oxidant. In the presence of diethyl acetylenedicarboxylate, the salt IIIc failed to give the expected adduct (Xc).

The prerequisite for the formation of the enethiols, V, is the presence of a methylene group adjacent to the sulfur atom in III, or Y=H. The treatment of IIId or IIIe (Y=Ph) must, therefore, take a different course (Scheme 3). When IIId was treated with sodium hydride in THF, an enediamine (VIId) was obtained in a 44% yield, along with elemental sulfur (22%), II(42%), and an oil whose IR suggested the possibility of its being VIIId. Similarly, IIIe gave VIIe (31%), and an olefinic ester (VIIIe) which was a *ca.* 1 : 1 mixture of (*Z*) and (*E*) isomers.



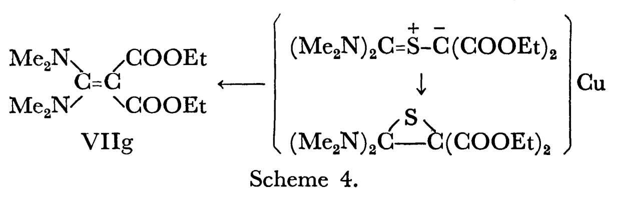
Scheme 3.

The formation of VIId and VIIe can be explained as is shown in Scheme 3. The ylides, Id and Ie, may be cyclized to thiiranes, which are then decomposed spontaneously to VIId or VIIe and sulfur. In the presence of dimethyl acetylenedicarboxylate, no addition product was obtained and the product distributions were not affected. These results indicate that the decomposition of Id and Ie is a fast process.

A possible account of the formation of VIIIe is given also in Scheme 3. In analogy to the recorded thermal decomposition of methylphenylsulfonium phenacylide to tribenzoylcyclopropane,[6] the nucleophilic ylide (Ie) may attack the salt IIIe to afford XV, whose Hofmann elimination then gives VIIIe. Such an intermolecular reaction of the labile ylide Ie might be possible if Ie is generated close enough to the unchanged IIIe.

Finally, under appropriate conditions, the sulfides, IXa, IXc, and IXf, were obtained from IIIa, IIIc, and IIIf respectively. The S-benzylthiouronium salt, IIIf (R=Ph, Y=H), gave IXf and II upon treatment with sodium hydride, neither VIf nor VIIf and was obtained (see Table 1). The direct precursor of IX is not yet known.

Reaction of II with Diazomalonate. A cyclohexane solution of II and diethyl diazomalonate was heated



Scheme 4.

Table 4. Spectral features of β,β-bis(dimethylamino)-α,β-unsaturated carbonyl compounds XVI

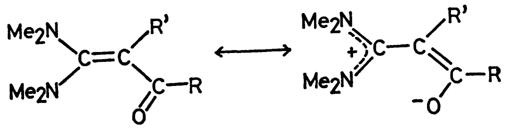
Compd.	R	R′	IR ($\nu_{C=O}$ cm^{-1})	NMR (δ NMe$_2$ in CDCl$_3$)$^{c)}$
XIIa	OEt	H	1675$^{a)}$	2.79 (s, 6H), 2.87 (s, 6H)
XIVb	OMe	SMe	1651$^{a)}$	2.88 (s, 12H)
XIVa	OEt	SMe	1645$^{b)}$	2.92 (s, 12H)
VIa	OEt	-S-S-	1633$^{b)}$	2.96 (s, 12H)
VIId	OEt	Ph	1642$^{b)}$	2.94 (s, 12H)
XIIc	Ph	H	1513$^{b)}$	2.96 (s, 12H)
VIc	Ph	-S-S-	1510$^{b)}$	2.85 (s, 12H)
VIIg	OEt	COOEt	1658, 1625$^{b)}$	2.97 (s, 12H)

a) Obtained in neat liquid film. b) Obtained in KBr tablet. c) Measured at 23 °C.

under reflux for 12 hr in the presence of copper powder to afford VIIg in a 25% yield. An attempted photoreaction[7)] of the components failed. No nitrogen evolution was observed in the absence of the copper catalyst in the dark, either.

We are tempted to assume the intermediacy of a copper carbenoid[8)] (Scheme 4), but the exact nature of catalysis is not yet known. Copper salts or chelates gave much inferior yields of VIIg. Copper powder may effectively facilitate the desulfurization step.

Characteristic Spectra of Enediamines (XVI). Table 4 shows the spectral features of XVI, including the wave numbers of the carbonyl stretching and the NMR signals of the dimethylamino groups measured in deuteriochloroform at room temperature. The implications of these data may be summarized as follows. 1) The CO stretching vibrations occur at lower frequencies than those of regular α,β-unsaturated esters or ketones. 2) The *N*-methyl proton signals appear approximately 0.5—0.7 ppm downfield from ordinary ones.[9)] 3) Though the two dimethylamino groups should be nonequivalent on the assumption of a restricted rotation about the C=C bond,[10)] the chemical shifts of all the dimethylamino protons coincided except for those of XIIa. Such characteristic data point to the idea that the contribution of a betain form, XVI′, is predominant in contrast to usual α,β-unsaturated carbonyl compounds.



XVI XVI′

Experimental

All the mps and bps are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyôto University. The NMR spectra were taken with a JEOL C-60H spectrometer at 60 MHz or a Varian HA 100 spectrometer at 100 MHz. The mass spectra were obtained on a Hitachi RMU-6L spectrometer, a Hitachi RMU-6D spectrometer, or a Hitachi RMS-4 spectrometer. The high-resolution mass spectrum of VIb was obtained on a JMS-OlSG spectrometer.

S-*Ethoxycarbonylmethyl*-N,N,N′,N′-*tetramethylthiouronium Bromide (IIIa).* A solution of II (6.7 g, 50 mmol) and ethyl bromoacetate (8.4 g, 50 mmol) in acetone (100 ml) was stirred for 3 hr at room temperature to give white precipitates of IIIa (13.8 g, 92%). The spectral data and the elemental analyses of IIIa are shown in Tables 2 and 3.

The other thiouronium salts (IIIb—IIIf) were prepared in a similar way.

Ethyl 3,3-Bis(dimethylamino)-2-[1,2-bis(ethoxycarbonyl)vinylthio]acrylate (Xa). Into a suspension of IIIa (3.0 g, 20 mmol) and diethyl acetylenedicarboxylate (3.4 g, 20 mmol) in THF (70 ml), triethylamine (3.0 g, 30 mmol) was added, drop by drop, under a nitrogen atmosphere at room temperature. The reaction mixture was then stirred for 12 hr, diluted with water (200 ml), and repeatedly extracted with chloroform. The combined extracts were washed with water, dried (magnesium sulfate), and concentrated *in vacuo.* The residual oil was purified by column chromatography (silica gel, chloroform) to yield an oil which solidified upon trituration with ether. Recrystallization from ethanol-hexane gave Xa (2.8 g, 73%); mp 91—92 °C. IR (KBr): 1733, 1705, 1660, 1590, 1530, 1150, 1069, 770 cm^{-1}. NMR (δ, CDCl$_3$): 1.22 (t, 3H), 1.24 (t, 3H), 1.33 (t, 3H), 2.86 (s, 12H), 4.12 (q, 2H), 4.16 (q, 2H), 4.30 (q, 2H), 5.50 (s, 1H). The mass spectrum of Xa is shown in Fig. 1. Found: C, 52.9; H, 7.3%. Calcd for $C_{17}H_{28}N_2O_6S$: C, 52.6; H, 7.3%.

Similarly, methyl 3,3-bis(dimethylamino)-2-[1,2-bis(ethoxycarbonyl)vinylthio]acrylate (Xb) was obtained in a 70% yield as colorless crystallines; mp 79—80 °C (recrystallized from ethanol-hexane). IR (KBr): 1740, 1705, 1661, 1590, 1529, 1150, 1069, 770 cm^{-1}. NMR (δ, CDCl$_3$): 1.24 (t, 3H) 1.35 (t, 3H), 2.88 (s, 12H), 3.68 (s. 3H), 4.12 (q, 2H), 4.30 (q, 2H), 5.56 (s, 1H). The mass spectrum of Xb is shown in Fig. 1. Found: C, 51.6; H, 7.1%. Calcd for $C_{16}H_{26}N_2O_6S$: C, 51.3; H, 7.0%.

Di[2,2-bis(dimethylamino)-1-(ethoxycarbonyl)vinyl] Disulfide (VIa). To a stirred suspension of IIIa (6.0 g, 20 mmol) in THF (200 ml), sodium hydride (0.90 g of a 52% dispersion in mineral oil, 20 mmol) was added in one portion. The reaction mixture was stirred until the evolution of hydrogen had stopped (*ca.* 3 hr). After it had then been filtered, the filtrate was evaporated to give a yellow solid of VIa, which was subsequently washed with ether. The crude product (3.6 g, 83%) was recrystallized from ethanol; mp 142—143 °C. IR(KBr): 1633, 1510, 1050, 766 cm^{-1}. NMR (δ, CDCl$_3$): 1.23(t, 6H), 2.96 (s, 24H), 4.07 (q, 4H). Found: C, 49.6; H, 8.1; S, 14.8%. Calcd for $C_{18}H_{34}N_4O_4S_2$: C, 49.8; H, 7.9; S, 14.7%.

Similarly, di[2,2-bis(dimethylamino)-1-(methoxycarbonyl)-vinyl] disulfide (VIb) was obtained in a 42% yield as a yellow solid; mp 163—164 °C (from ethanol). IR (KBr): 1640, 1515, 1056, 767 cm^{-1}. NMR (δ, CDCl$_3$): 2.95 (s, 24H), 3.57 (s, 6H). The high-resolution mass spectrum of VIb is shown is Fig. 2. Found: C, 47.3; H, 7.6; S, 15.6%. Calcd for $C_{16}H_{30}N_4O_4S_2$: C, 47.3; H, 7.4; S, 15.7%.

thyl 3,3-Bis(dimethylamino)-2-(methylthio)acrylate (XIVa). THF (100 ml) was completely degassed *in vacuo* (1 mmHg) for

3 hr at −60 °C. To this, sodium hydride (1.0 g of a 51.9% dispersion in mineral oil, 22 mmol) and IIIa (2.3 g, 7.7 mmol) were added successively under a nitrogen atmosphere at room temperature. After stirring for 12 hr, methyl iodide (1.5 g, 106 mmol) was added, drop by drop. The mixture was then stirred for 3 hr and filtered, after which the filtrate was concentrated *in vacuo* to afford an oil. Chromatography on a silica-gel column with benzene, ether, and ethanol as the eluents gave II (84 mg, 8.3%), VIa (200 mg, 12%), and XIVa as a colorless oil which solidified upon trituration with hexane at −50 °C (300 mg, 17%). Recrystallization from hexane gave an analytical sample; mp 31—32 °C. IR (KBr): 1645, 1517, 1210, 1056, 767 cm^{-1}. NMR (δ, CCl_4): 1.27 (t, 3H), 2.03 (s, 3H), 2.78 (s, 6H), 2.88 (s, 6H), 4.07 (q, 2H). Mass spectrum (*m/e*): 232 (M$^+$). Found: C, 52.4; H, 9.1%. Calcd for $C_{10}H_{20}N_2O_2S$: C, 51.7; H, 8.7%.

Methyl 3,3-Bis(dimethylamino)-2-(methylthio)acrylate (XIVb). Sodium hydride (3.0 g of a 51.9% dispersion in mineral oil, 65 mmol) was washed three times with hexane and then suspended in DMF (100 ml). To this, *S*-methoxycarbonylmethyl-*N,N,N',N'*-tetramethylthiouronium bromide (IIIb) (5.7 g, 20 mmol) was added in small portions under a nitrogen atmosphere at room temperature. After the evolution of hydrogen had ceased (*ca.* 1 hr), methyl iodide (5.0 g, 35 mmol) was added, drop by drop. The mixture was then stirred for 1 hr, diluted with water (200 ml), neutralized by the addition of ammonium chloride, and extracted with chloroform. After drying (magnesium sulfate), the combined extracts were distilled *in vacuo* to yield XIVb as a colorless oil (320 mg, 7.3%); bp 88—90 °C/0.07 mmHg. IR (neat): 1651, 1525, 1210, 1060, 770 cm^{-1}. NMR (δ, CCl_4): 2.03 (s, 3H), 2.81 (s, 6H), 2.89 (s, 6H), 3.61 (s, 3H). Found: C, 49.6; H, 8.6%. Calcd for $C_9H_{18}N_2O_2S$: C, 49.5; H, 8.3%.

Ethyl 3,3-Bis(dimethylamino)acrylate (XIIa). To a solution of VIa (2.2 g, 5 mmol) in ethanol (100 ml), Raney nickel (W-2) (36 g) was added. The mixture was stirred at room temperature for 2 hr and filtered, and the filtrate was distilled *in vacuo* to afford XIIa as a colorless oil (1.4 g, 76%); bp 76.5—77 °C/1 mmHg. IR (neat): 1675, 1555, 1158, 1050, 780 cm^{-1}. NMR (δ, $CDCl_3$): 1.26 (t, 3H), 2.79 (s, 6H), 2.87 (s, 6H), 3.96 (s, 1H), 4.09 (q, 2H). Mass spectrum (*m/e*): 186 (M$^+$). Found: C, 57.5; H, 10.0%. Calcd for $C_9H_{18}N_2O_2$: C, 58.0; H, 9.7%.

Similarly, the desulfurization of VIb afforded methyl 3,3-bis(dimethylamino)acrylate (XIIb) as a colorless oil in a 68% yield; bp 87—88 °C/4 mmHg. IR (neat): 1675, 1550, 1120, 1054, 779 cm^{-1}. NMR (δ, $CDCl_3$): 2.81 (s, 6H), 2.88 (s, 6H), 3.62 (s, 3H), 3.96 (s, 1H). Mass spectrum (*m/e*): 172 (M$^+$). Found: C, 55.6; H, 9.6%. Calcd for $C_8H_{16}N_2O_2S$: C, 55.8; H, 9.4%.

Desulfurization of Xa. Raney nickel (W-2) (2 g) was added to a solution of Xa (250 mg, 0.64 mmol) in ethanol (50 ml). After stirring for 15 min at room temperature, the mixture was filtered and the filtrate was concentrated to afford an oil, which consisted of diethyl succinate and XIIa. Identification was made by a comparison of the IR spectra and the retention times of glc (High vacuum silicone grease 30%) with those of authentic samples. The yield of diethyl succinate, as calculated from the peak area in glc, was 80%, while that of XIIa was 56%.

Similarly, the desulfurization of Xb with Raney nickel afforded diethyl succinate (68%) and XIIb (40%).

Ethyl N,N-*Dimethylmalonamidate (XIII).* Ethyl hydrogen malonate (3.5 g, 26 mmol) was added, drop by drop, to thionyl chloride (20 ml); the solution was heated at 50 °C for 2 hr and then under reflux for 1 hr. After cooling, the solution was concentrated *in vacuo* to yield ethyl chloroformylacetate.[11] An excess of anhydrous dimethylamine gas was passed through a solution of ethyl chloroformylacetate in ether (50 ml) to give white precipitates. The reaction mixture was then filtered, and the filtrate was distilled *in vacuo* to yield XIII as a colorless oil (4.5 g, 94% based on ethyl hydrogen malonate); bp 94—96 °C/1 mmHg. IR (neat): 1735, 1645, 1250, 1170, 1030 cm^{-1}. NMR (δ, CCl_4): 1.30 (t, 3H) 2.91 (s, 3H), 3.02 (s, 3H), 3.32 (s, 2H), 4.16 (q, 2H). Found: C, 52.7; H, 8.2; N, 8.8%. Calcd for $C_7H_{13}NO_3$: C, 52.8; H, 8.2; N, 8.8%.

Hydrolysis of XIIa. A solution of XIIa (0.48 g, 2.6 mmol) and *p*-toluenesulfonic acid (5 mg) in THF-water (1 : 1, 50 ml) was stirred at room temperature for 3 days and then extracted four times with chloroform (70 ml). The extracts were combined, shaked with an aqueous sodium bicarbonate solution, washed with water, dried (magnesium sulfate), and concentrated *in vacuo* to give an oil which consisted of XIIa and XIII. Identification was made by a comparison of the IR spectra and the retention times of glc (Polyethylene glycol-$AgNO_3$ 30%) with those of authentic samples.

Di[2,2-bis(dimethylamino)-1-benzoylvinyl] Disulfide (VIc). Sodium hydride (0.50 g of 51.9% dispersion in mineral oil, 11 mmol) was washed with *n*-hexane and then suspended in DMSO (50 ml). Into this, *S*-phenacyl-*N,N,N',N'*-tetramethylthiouronium bromide (IIIc) (3.3 g, 10 mmol) was stirred in small portions at room temperature. After the evolution of hydrogen had stopped (*ca.* 30 min), the brown-red solution was diluted with water (100 ml), and extracted four times with chloroform (150 ml); the combined extracts were then washed three times with water (100 ml), dried (magnesium sulfate), and concentrated *in vacuo* to give an oil. This oil solidified on trituration with ether to yield a yellow solid of VIc (1.56 g, 64%). Recrystallization from ethanol upon the addition of ether gave an analytical sample; mp 192—195 °C. IR (KBr): 1600, 1590, 1510, 1400, 710, 660 cm^{-1}. NMR (δ, $CDCl_3$): 2.85 (s, 24H), 7.2—7.6 (m, 10H). Found: C, 62.4; H, 7.1%. Calcd for $C_{26}H_{34}N_4O_2S_2$: C, 62.6; H, 6.9%.

Reaction of S-[*α-(Methoxycarbonyl)benzyl*]-N,N,N',N'-*tetramethylthiouronium Bromide (IIIe) with Sodium Hydride.* Sodium hydride (0.50 g of a 51.9% disperion in mineral oil, 11 mmol) was suspended in THF (50 ml). To this, IIIe (3.6 g, 10 mmol) was added under a nitrogen atmosphere at room temperature. The mixture was stirred for 5 days and then filtered, after which the filtrate was concentrated *in vacuo* to afford an oil, which was subsequently chromatographed on a silica gel column. From the benzene eluent, we obtained a mixture of dimethyl 2,3-diphenylfumarate and dimethyl 2,3-diphenylmaleate (VIIIe) as a colorless solid (0.17 g, 12%). The (Z) and (E) isomers could not be separated, but the intensities of the methoxy protons in NMR indicated that the ratio of the (Z) to the (E) isomers was *ca.* 1. IR (nujol): 1720, 1500, 1275, 1225, 1210, 1010, 725, 700 cm^{-1}. NMR (δ, CCl_4): 3.46 (s, 3H), 3.77 (s, 3H), 7.0—7.4 (m, 10H). Mass spectrum (*m/e*): 296 (M$^+$). Recrystallization from ethanol gave an analytical sample; mp 103—107 °C.[12] Found: C, 72.9; H, 5.3%. Calcd for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4%.

The benzene–ether eluent (4 : 1) gave II (0.43 g, 34%), which was identified by a comparison of its IR spectrum with that of authentic sample.

From the ether eluent, we obtained methyl 3,3-bis(dimethylamino)-2-phenylacrylate (VIIe) (0.77 g, 31%) as a colorless solid. Recrystallization from hexane gave an analytical solid. Recrystallization from hexane gave an analytical sample; mp 69 °C. IR (KBr): 1632, 1520, 1180, 1050, 770, 690 cm^{-1}. NMR (δ, CCl_4): 2.75 (broad s, 12H), 3.57 (s, 3H), 6.7—7.2 (m, 5H). Found: C, 67.9; H, 8.4; N, 11.2%. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.7; H, 8.1; N, 11.3%.

Reaction of S-[α-*(Ethoxycarbonyl)benzyl*]-N,N,N′,N′-*tetramethylthiouronium Bromide (IIId) with Sodium Hydride.* To a stirred suspension of sodium hydride (0.50 g of a 51.9% dispersion in mineral oil, 11 mmol) in THF (50 ml), IIId (4.0 g, 11 mmol) was added under a nitrogen atmosphere at room temperature. The mixture was then stirred for 24 hr and filtered, after which the filtrate was concentrated *in vacuo* to afford an oil, which was subsequently chromatographed on a silica gel column. The benzene eluent gave elemental sulfur (74 mg, 22%) and an oil (0.57 g) whose IR (neat, 1725, 1690, 1600, 1450, 1370, 1200, 1010, 720, 680 cm^{-1}) suggested the presence of Ph- and EtOOC- groups. The benzene–ether eluent (4 : 1) gave II (0.59 g, 42%). The ether eluent gave ethyl 3,3-bis(dimethylamino)-2-phenylacrylate (VIId) as a colorless solid (1.23 g, 44%); mp 63 °C (from hexane). IR (KBr): 1642, 1514, 1290, 1170, 1050, 770, 695 cm^{-1}. NMR (δ, CCl_4): 1.22 (t, 3H), 2.74 (s, 12H), 4.05 (q, 2H), 6.7—7.2 (m, 5H). Found: C, 68.9; H, 8.4%. Calcd for $C_{15}H_{22}N_2O_2$: C, 68.8; H, 8.5%.

Treatment of IIIa with Triethylamine. To a suspension of IIIa (6.0 g, 20 mmol) in THF (100 ml), triethylamine (6.0 g, 60 mmol) was added, drop by drop, under a nitrogen atmosphere at room temperature. The mixture was stirred for 2 weeks, diluted with water (300 ml), and extracted with chloroform (200 ml). The combined extracts were dried (magnesium sulfate) and then concentrated *in vacuo* to give an oil. Chromatography on a silica gel column, with benzene, ether, and methanol as eluents, gave predominantly diethyl thiodiglycolate (IXa) as a colorless oil; bp 89 °C/2 mmHg (lit,[13] bp 105 °C/3 mmHg) (0.70 g, 34%). IR (neat): 1730, 1270, 1150, 1025 cm^{-1}. NMR (δ, CCl_4): 1.30 (t, 6H), 3.32 (s, 4H), 4.11 (q, 4H). Found: C, 46.8; H, 7.1; S, 15.8%. Calcd for $C_8H_{14}O_4S$: C, 46.6; H, 6.8; S, 15.5%.

The other products were II (0.87 g, 29%) and VIa (0.24 g, 5.5%), which were identified by a comparison of their IR spectra with those of authentic samples.

Treatment of IIIc with Triethylamine. To a stirred suspension of IIIc (9.9 g, 30 mmol) in THF (100 ml), triethylamine (10 g, 0.10 mol) was added, drop by drop, under a nitrogen atmosphere, after which the mixture was stirred at room temperature for 24 hr. Working up the product, followed by chromatographic separation on a silica gel column with benzene and ether as eluents, yielded diphenacyl sulfide (IXc) (1.12 g, 28%); mp 74—75 °C (from ethanol) (lit,[14] 74 °C). IR (KBr): 1690, 1595, 1450, 985, 750, 685, 645 cm^{-1}. NMR (δ, $CDCl_3$): 4.00 (s, 4H), 7.2—8.1 (m, 10H). Found: C, 71.5; H, 5.2%. Calcd for $C_{16}H_{14}N_2S$: C, 71.1; H, 5.2%.

Another product, II (1.90 g, 48%), was identified by comparison of its spectrum with that of an authentic specimen.

Treatment of S-*Benzyl*-N,N,N′,N′-*tetramethylthiouronium Bromide (IIIf).* Sodium hydride (0.25 g of a 51.9% dispersion in mineral oil, 55 mmol) was washed with *n*-hexane and then suspended in THF (30 ml). To this stirred mixture, IIIf (1.75 g, 50 mmol) was added under nitrogen. After the mixture had been stirred for 5 days at roon temperature and filtered, the filtrate was concentrated *in vacuo* to give an oil. Chromatography on a silica gel column, with benzene and ether as eluents, gave dibenzyl sulfide (IXf) 124 mg, 23%); mp 45—46 °C (lit,[15] mp 49 °C). IR (neat): 1600, 1598, 1455, 755, 683 cm^{-1}. NMR (δ, CCl_4): 3.47 (s, 4H), 7.17 (s, 10H). Mass spectrum (m/e): 214 (M^+).

The by-product was tetramethylthiourea II (68 mg, 8.5%).

Diethyl Bis(dimethylamino)methylenemalonate (VIIg). To a stirred mixture of II (6.6 g, 50 mmol) and copper powder (1.0 g) in cyclohexane (50 ml), diethyl diazomalonate (1.86 g, 10 mmol) was added at room temperature under nitrogen. The reaction mixture was then heated under reflux for 12 hr and filtered, after which the filtrate was evaporated *in vacuo* to give an oil, which was chromatographed on a silica gel column. After the elution of II with ether, the residue was eluted with chloroform. The combined extracts were dried (magnesium sulfate) and concentrated *in vacuo* to afford an oil, which solidified upon trituration with ether at −30 °C to yield a colorless solid of VII g (0.65 g, 25%); mp 64 °C (from *n*-hexane) (lit,[16] mp 67—68 °C). IR (KBr): 1658, 1625, 1560, 1520, 1275, 1210, 1060, 905, 796 cm^{-1}. NMR (δ, $CDCl_3$): 1.28 (t, 6H), 2.97 (s, 12H), 4.17 (q, 4H). Found: C, 55.9; H, 8.7; N, 10.9%. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.8; H, 8.6; N, 10.7%.

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