New reaction of thiocarbonyl ylides. Interaction of *S*-alkyl-*N*,*N*-dimethylthiobenzimidium salts with activated acetylene derivatives leading to (*E*,*E*)-divinyl sulfides

I. V. Magedov,[a] N. M. Przheval'skii,[a] D. S. Yufit,[b] and V. N. Droz'd[a]**

[a]*K. A. Timiryazev Agricultural Academy, Department of Organic Chemistry, 49 ul. Timiryazevskaya, 127550 Moscow, Russian Federation. Fax: 007 (095) 976 1820*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: 007 (095) 135 5085*

The reaction of thiocarbonyl ylides with activated acetylene derivatives gives (*E*,*E*)-divinyl sulfides in good yields. The reaction mechanism is discussed and evidence in favor of the formation of a thiirane intermediate is presented.

Key words: (*E*,*E*)-divinyl sulfides; thiiranes; thiocarbonyl ylides; acetylene derivatives.

Thiocarbonyl ylides are known to be highly reactive compounds. The following reactions have been described for them: intramolecular 1,3-electrocyclization yielding thiiranes;[1] dimerization to 1,4-dithianes;[2] 1,5-electrocyclization,[3,4] and 1,3-dipolar cycloaddition[5] to give five-membered sulfur-containing heterocyclic compounds.

We found a new reaction (Scheme 1) of thiocarbonyl ylides with activated alkynes to yield (*E*,*E*)-divinyl sulfides (see the preliminary communication[6]).

Results and Discussion

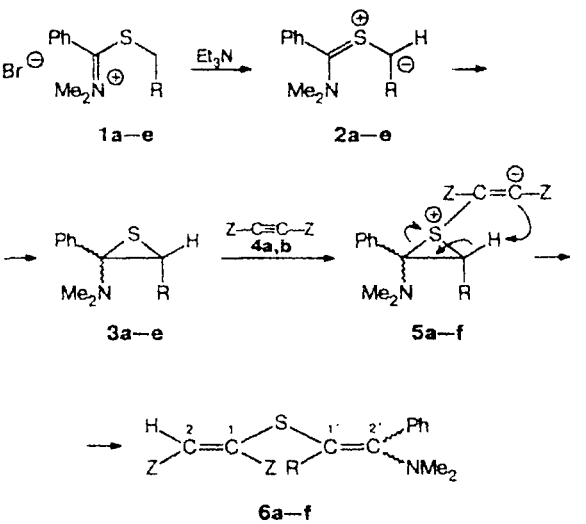
S-Alkyl-*N*,*N*-dimethylthiobenzimidium salts (**1a—e**) with an electron-withdrawing group in the methyl *S*-substituent react with acetylene derivatives (**4a,b**), which contain two electron-withdrawing substituents, in the presence of Et_3N to give (*E*,*E*)-divinyl sulfides (**6a—e**) in high yields (see Scheme 1).

The reaction scheme proposed by us includes: (1) deprotonation of *S*-alkyl-*N*,*N*-dimethylthiobenzimidium salts **1a—e** to give thiocarbonyl ylides (**2a—e**); (2) 1,3-electrocyclization of the latter to thiiranes (**3a—e**); (3) nucleophilic addition of thiiranes **3a—e** to activated acetylene derivatives **4a,b** resulting in the formation of zwitterions (**5a—f**), and (4) an intramolecular suprafacial shift of a proton accompanied by opening of the thiirane ring in zwitterion **5** to yield divinyl sulfides **6a—f** having the (*E*)-configuration at the C(1)=C(2) double bond.

A similar mechanism including the addition of sulfides to acetylene derivatives has been suggested for the reaction of alkyl allyl sulfides with alkyl propiolates in the presence of Lewis acids to give alkyl α-alkylthio-β-allylacrylates.[7,8]

For this reaction to occur, an electron-donating group (NMe_2) and strong electron-withdrawing groups (COPh, CO_2Me, $C_6H_4NO_2$) need to be present in the

Scheme 1



R = COPh (**1a**, **6a,b**); CO_2Me (**1b**, **6c**); $C_6H_4NO_2$-*p* (**1c**, **6d**); $CH{=}CHCO_2Me$ (**1d**, **6e**); $CMe{=}CHCO_2Me$ (**1e**, **6f**);
Z = COPh (**4a**, **6b**); CO_2Me (**4b**, **6a,c—f**)

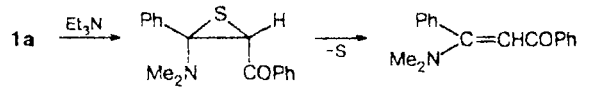
Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 4, pp. 791—795, April, 1997.

1066-5285/97/4604-0759 $18.00

corresponding positions of the thioimidium salt **1**. For example, replacement of the dimethylamino group by a weaker donor (SMe) results in a sharp decrease in the nucleophilicity of the sulfur atom of the thiirane ring, and this prevents the formation of zwitterion **5**. On the other hand, the replacement of the above-mentioned electron-withdrawing groups by a weaker acceptor (the carbon—carbon double bond in *S*-allyl-*N*,*N*-dimethylthiobenzimidium bromide) decreases the acidity of the protons of the CH_2—R group, and hence, thioimidium salt **1** is not deprotonated to thiocarbonyl ylide **2**, but, instead, it is dealkylated virtually quantitatively to the initial *N*,*N*-dimethylthiobenzamide.

The attempts to isolate the key intermediate, thiirane **3a**, failed; this is due to the instability of derivatives of α,β-thioglycidic acids in the presence of bases (elimination of the sulfur atom).[9,10] When the reaction of *N*,*N*-dimethyl-*S*-phenacylthiobenzimidium bromide **1a** with Et_3N was carried out in the absence of dimethyl acetylenedicarboxylate, enaminone (**7**) (72%) was isolated in addition to the dealkylation product, *N*,*N*-dimethylthiobenzamide (26%) (Scheme 2). The structure of enaminone **7** was confirmed by the fact that it was identical with an authentic sample prepared by a known procedure.[11]

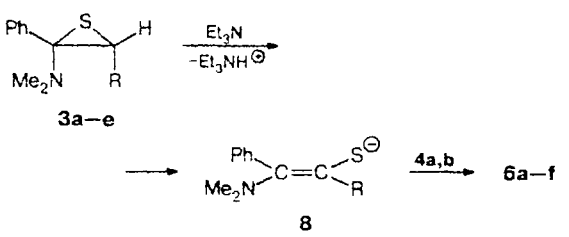
Scheme 2



3a **7**

The fact that monoactivated acetylene derivatives (ethyl propiolate) and activated alkenes (*N*-phenylmaleimide) do not enter into this reaction makes it possible to rule out the alternative mechanism involving the rearrangement of thiirane **3** to 1-alkenethiolates (**8**) through the action of a base and the subsequent addition of the latter to acetylene derivative **4** (Scheme 3), because this is at variance with the known data on the easy addition of thiolates to activated double and triple bonds.[12] Moreover, in our case, the addition to the triple bond occurs *cis*-stereospecifically, whereas nucleophilic addition of thiols to dimethyl acetylenedicarboxylate usually occurs *trans*-stereoselectively.[12]

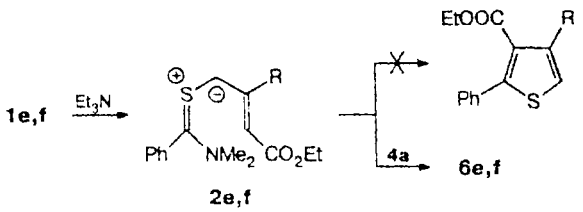
Scheme 3



The stereospecific formation of only (*E*)-isomers with respect to the C(1)=C(2) bond can be reasonably explained by a concerted six-electron rearrangement in the intermediate zwitterion **5** (see Scheme 1). At the same time, despite the fact that 1,3-electrocyclization of thiocarbonyl ylides to thiiranes occurs stereospecifically,[13] deprotonation of salts **1** is controlled by thermodynamic factors, which generally results in a mixture of (*Z*)- and (*E*)-isomers of thiocarbonyl ylides **2**, thiiranes **3**, and, correspondingly, (*Z*)- and (*E*)-isomers of divinyl sulfides **6** with respect to the C(1′)=C(2′) bond: **6a** (1 : 0), **6b** (1 : 0), **6c** (11 : 1), **6d** (2 : 1), **6e** (4 : 1), and **6f** (3 : 1).

It may be expected that thiocarbonyl ylides **2e,f**, which contain an additional *endo*-double bond, would undergo 1,5-electrocyclization to thiophenes (Scheme 4). However, in the absence of activated acetylene derivatives **4a,b**, this scheme could not be accomplished. Instead, these compounds smoothly undergo 1,3-electrocyclization to give thiiranes **3e,f**. In the presence of dimethyl acetylenedicarboxylate, the latter are converted into divinyl sulfides **6e,f** in good yields (see Schemes 1 and 4).

Scheme 4



The molecular structure of one of the divinyl sulfides, (*E*,*E*)-1′-benzoyl-2′-dimethylamino-1,2-di(methoxycarbonyl)-2′-phenyldivinyl sulfide (**6a**), was determined by an X-ray structural study. The general view of molecule **6a** is shown in Fig. 1, and the bond lengths and bond angles are presented in Tables 1 and 2, respectively. Previously, only one divinyl sulfide derivative, (*Z*,*Z*)-3,3′-thiobis(1,3-diphenylprop-2-en-1-one) (**9**), has been studied by X-ray diffraction.[14] The S—C bond lengths in molecules **6a** and **9** are virtually identical, while the geometric parameters of the vinyl fragments (which are equivalent in **9**) are substantially dissimilar. In the molecule of **6a**, the C(1)=C(2) bond is localized and its length (1.325(6) Å) is close to that calculated for methyl vinyl sulfide (1.311 Å),[15] although it is somewhat shorter than that found in **9** (1.348 Å). The orientation of this bond corresponds to the energetically most favorable[15] *syn*-conformation: the C(7)S(1)C(1)C(2) torsional angle is 4.2°. The terminal methoxycarbonyl group C(3)O(1)O(2)C(4) lies in the plane of the C(1)=C(2) double bond and is obviously involved in conjugation with its π-system, whereas the second MeOCO group does not participate in conjugation, because its plane forms a dihedral angle of 94.6° with the plane of the

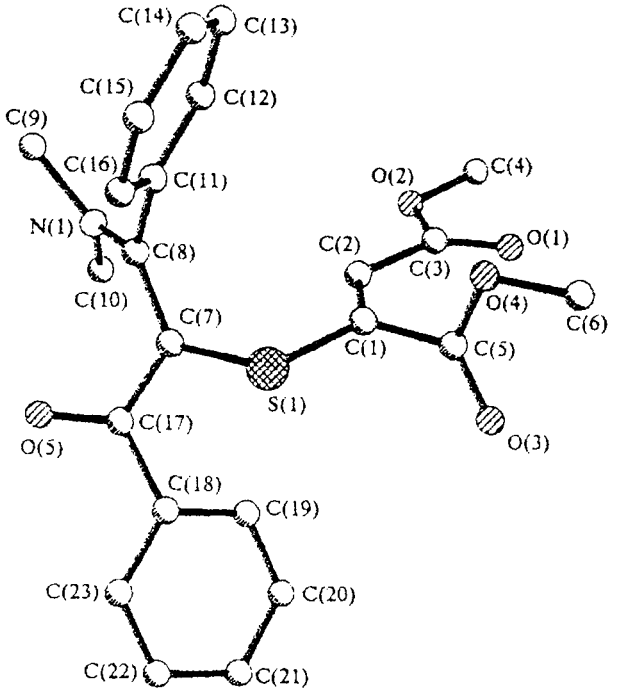
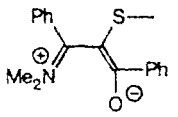


Fig. 1. The structure of molecule **6a**.

double bond. This is in agreement with the fact that the C(2)—C(3) and C(1)—C(5) bond lengths are markedly different. The most interesting feature of molecule **6a** is the geometry of the second vinyl group, C(7)=C(8), which is substantially deflected from the plane of the C(1)S(1)C(7) sulfide bridge (the C(1)S(1)C(7)C(8) torsional angle is −74.8°). The C(7)=C(8) double bond is considerably lengthened and twisted: the S(1)C(7)C(17) and N(1)C(8)C(11) planes form an angle of 29.0°. Structures of this kind are typical of strongly polarized ethenes (see, for example, Refs. 16 and 17). In fact, in the molecule of **6a**, the O(5)=C(17) carbonyl bond is substantially longer, with a length equal to 1.247(6) Å and the N(1)—C(8) bond is, conversely, shorter, with a length of 1.337(6) Å. This indicates that a bipolar form makes quite a substantial contribution to the observed geometry of molecule **6a**.



Besides polarization of the C(7)=C(8) bond, steric factors also play an important role in the distortion of the molecular geometry: in spite of the substantial twisting around this bond, short intramolecular contacts, O(5)...N(1) 2.432(6), O(5)...C(10) 2.794(7), S(1)...C(11) 3.073(6), and S(1)...C(18) 3.133(6) Å, are also retained in molecule **6a**. The plane of the C(11)—C(16) benzene ring forms a dihedral angle of 111.1° with the plane of the dimethylamino group, while the plane of the second benzene ring, C(18)—C(23), forms an angle of 132.0° with the plane of the C(18)C(17)O(5)C(7) carbonyl group. In the crystal, molecules **6a** are bound only by weak van der Waals interactions.

Table 1. Bond lengths (*d*) in molecule **6a**

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(1)	1.753(6)	C(7)—C(17)	1.462(8)
S(1)—C(7)	1.754(4)	C(8)—C(11)	1.489(8)
O(1)—C(3)	1.210(8)	C(11)—C(12)	1.388(8)
O(2)—C(3)	1.325(6)	C(11)—C(16)	1.387(7)
O(2)—C(4)	1.457(8)	C(12)—C(13)	1.380(8)
O(3)—C(5)	1.195(7)	C(13)—C(14)	1.376(8)
O(4)—C(5)	1.329(7)	C(14)—C(15)	1.38(1)
O(4)—C(6)	1.452(6)	C(15)—C(16)	1.375(9)
O(5)—C(17)	1.247(6)	C(17)—C(18)	1.489(7)
N(1)—C(8)	1.337(6)	C(18)—C(19)	1.380(7)
N(1)—C(9)	1.453(6)	C(18)—C(23)	1.404(8)
N(1)—C(10)	1.457(7)	C(19)—C(20)	1.384(8)
C(1)—C(2)	1.325(6)	C(20)—C(21)	1.380(1)
C(1)—C(5)	1.497(7)	C(21)—C(22)	1.380(1)
C(2)—C(3)	1.471(9)	C(22)—C(23)	1.372(9)
C(7)—C(8)	1.403(7)		

Experimental

IR spectra were recorded in KBr on a Perkin—Elmer 577 spectrophotometer; ^{1}H NMR spectra were run on a Bruker AC 250 instrument using tetramethylsilane as the internal standard; mass spectra were obtained on a Varian MAT-311-A instrument. Acetonitrile was dried by distillation over P_2O_5.

Table 2. Bond angles (φ) in molecule **6a**

Angle	φ/deg	Angle	φ/deg
C(1)—S(1)—C(7)	105.7(2)	C(7)—C(8)—C(11)	121.4(4)
C(3)—O(2)—C(4)	116.0(5)	C(8)—C(11)—C(12)	120.0(4)
C(5)—O(4)—C(6)	115.3(4)	C(8)—C(11)—C(16)	121.0(5)
C(8)—N(1)—C(9)	122.9(4)	C(12)—C(11)—C(16)	118.9(5)
C(8)—N(1)—C(10)	122.8(4)	C(11)—C(12)—C(13)	120.2(5)
C(9)—N(1)—C(10)	114.1(4)	C(12)—C(13)—C(14)	120.3(6)
S(1)—C(1)—C(2)	126.8(4)	C(13)—C(14)—C(15)	119.7(6)
S(1)—C(1)—C(5)	109.9(3)	C(14)—C(15)—C(16)	120.2(5)
C(2)—C(1)—C(5)	123.4(5)	C(11)—C(16)—C(15)	120.5(6)
C(1)—C(2)—C(3)	123.6(5)	O(5)—C(17)—C(7)	120.3(4)
O(1)—C(3)—O(2)	124.6(6)	O(5)—C(17)—C(18)	118.4(5)
O(1)—C(3)—C(2)	124.6(5)	C(7)—C(17)—C(18)	121.3(4)
O(2)—C(3)—C(2)	110.8(5)	C(17)—C(18)—C(19)	121.9(5)
O(3)—C(5)—O(4)	124.5(5)	C(17)—C(18)—C(23)	118.2(5)
O(3)—C(5)—C(1)	123.3(5)	C(19)—C(18)—C(23)	119.4(5)
O(4)—C(5)—C(1)	112.1(4)	C(18)—C(19)—C(20)	120.3(6)
S(1)—C(7)—C(8)	118.6(4)	C(19)—C(20)—C(21)	119.9(6)
S(1)—C(7)—C(17)	117.5(3)	C(20)—C(21)—C(22)	120.1(6)
C(8)—C(7)—C(17)	122.6(4)	C(21)—C(22)—C(23)	120.3(6)
N(1)—C(8)—C(7)	122.3(5)	C(18)—C(23)—C(22)	119.9(6)
N(1)—C(8)—C(11)	116.2(4)		

Table 3. Coordinates ($\times 10^4$) and equivalent isotropic thermal factors U ($\times 10^3$) of nonhydrogen atoms in the structure of **6a**

Atom	x	y	z	U/Å^2
S(1)	344(1)	3062(1)	587(1)	36(1)
O(1)	−785(4)	1109(3)	2670(3)	60(2)
O(2)	1241(4)	1305(2)	3775(3)	58(2)
O(3)	−1656(4)	1382(3)	280(3)	60(2)
O(4)	−2308(3)	2439(2)	1094(3)	45(2)
O(5)	3948(4)	546(2)	891(3)	46(2)
N(1)	3463(4)	3920(3)	2759(3)	34(2)
C(1)	−61(5)	2322(3)	1380(4)	30(2)
C(2)	695(5)	2076(3)	2290(4)	37(2)
C(3)	83(7)	1449(4)	2913(4)	44(3)
C(4)	963(7)	677(4)	4450(5)	81(4)
C(5)	−1414(5)	1974(4)	869(4)	38(2)
C(6)	−3650(5)	2150(4)	614(5)	62(3)
C(7)	1988(4)	3341(3)	1210(3)	27(2)
C(8)	2293(5)	3918(3)	2030(4)	30(2)
C(9)	3966(5)	4674(4)	3406(4)	40(2)
C(10)	4390(5)	3198(3)	2914(4)	45(2)
C(11)	1293(5)	4521(3)	2170(4)	30(2)
C(12)	983(5)	4474(3)	3039(4)	37(2)
C(13)	31(5)	5015(4)	3160(4)	46(3)
C(14)	−607(5)	5613(4)	2428(4)	54(3)
C(15)	−293(6)	5670(4)	1567(4)	57(3)
C(16)	657(6)	5134(4)	1443(4)	44(2)
C(17)	2927(5)	3109(3)	722(3)	29(2)
C(18)	2702(4)	2344(3)	28(3)	31(2)
C(19)	2401(5)	1521(3)	294(4)	37(2)
C(20)	2327(5)	808(4)	−329(5)	43(2)
C(21)	2541(5)	922(4)	−1228(5)	49(3)
C(22)	2859(5)	1743(4)	−1493(4)	47(3)
C(23)	2957(5)	2450(4)	−871(4)	42(2)

Table 4. Coordinates ($\times 10^3$) and isotropic thermal factors U ($\times 10^2$) of hydrogen atoms in the structure of **6a**

Atom	x	y	z	U/Å^2
H(2)	159(4)	220(2)	262(3)	3(1)
H(41)	185(6)	64(4)	504(4)	11(2)
H(42)	91(6)	7(4)	419(4)	11(2)
H(43)	28(6)	91(4)	468(5)	13(2)
H(61)	−379(5)	150(3)	72(4)	8(2)
H(62)	−412(4)	241(3)	86(3)	5(1)
H(63)	−391(4)	218(3)	−21(4)	7(2)
H(91)	429(4)	445(3)	415(3)	5(1)
H(92)	483(4)	485(2)	343(3)	3(1)
H(93)	337(4)	515(3)	326(3)	5(1)
H(101)	483(4)	310(3)	365(3)	4(1)
H(102)	384(4)	267(3)	257(3)	4(1)
H(103)	497(4)	334(3)	256(3)	6(1)
H(12)	146(4)	400(3)	360(3)	5(1)
H(13)	−21(4)	497(3)	376(3)	5(1)
H(14)	−145(4)	601(3)	244(3)	6(1)
H(15)	−67(4)	610(3)	108(3)	6(2)
H(16)	94(4)	517(3)	93(3)	6(1)
H(19)	233(4)	143(3)	94(3)	3(1)
H(20)	211(5)	25(4)	−17(4)	6(2)
H(21)	247(4)	38(3)	−166(3)	4(1)
H(22)	293(5)	182(4)	−213(4)	8(2)
H(23)	319(4)	300(3)	−98(3)	4(2)

The X-ray diffraction experiment was carried out using a Siemens P3/PC automatic diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning, θ ≤ 25°).

Yellow crystals of **6a** ($C_{23}H_{23}NO_5S$) (from acetonitrile) were monoclinic; at −40 °C, a = 10.894(3), b = 15.213(5), c = 14.192(4) Å, β = 110.15(2)°, Z = 4, space group $P2_1/n$. The unit cell parameters and the intensities of the 2796 independent reflections, 1526 of which with $I \geq 2\sigma(I)$ were used to solve and refine the structure, were measured using the diffractometer. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all of the nonhydrogen atoms. All of the H atoms identified from the Fourier differential synthesis were refined isotropically. The final residual factors were R = 0.048, R_w = 0.042. All calculations were carried out on an IBM PC/AT using the SHELX PLUS program package. The coordinates of nonhydrogen atoms are listed in Table 3, those of hydrogen atoms are given in Table 4.

***S*-Alkyl-*N*,*N*-dimethylthiobenzimidium bromides (1).** A solution of *N*,*N*-dimethylthiobenzamide (10 mmol) and an alkylating reagent (11 mmol) in acetonitrile (10 mL) was refluxed for 6 h and cooled. The solvent was evaporated *in vacuo*, and the residue was crystallized from an ether—acetonitrile mixture.

***N*,*N*-Dimethyl-*S*-phenacylthiobenzimidium bromide (1a).** Yield 86%, m.p. 135—137 °C. Found (%): C, 55.95; H, 4.92; N, 3.80; S, 8.64. $C_{17}H_{18}BrNO_4S$. Calculated (%): C, 56.05; H, 4.98; N, 3.85; S, 8.8. ^{1}H NMR (CD_3CN), δ: 3.33 and 3.78 (both s, 6 H, N—Me); 4.52 (s, 2 H, CH_2); 7.40—7.68 (m, 10 H, arom. H).

***N*,*N*-Dimethyl-*S*-(methoxycarbonylmethyl)thiobenzimidium bromide (1b).** Yield 80%, m.p. 160—162 °C. Found (%): C, 45.29; H, 5.07; N, 4.83; S, 9.63. $C_{12}H_{16}BrNO_6S$. Calculated (%): C, 45.29; H, 5.06; N, 4.40; S, 10.08. ^{1}H NMR ($CDCl_3$), δ: 3.30 (s, 3 H, N—Me); 3.30 (s, 3 H, O—Me); 3.56 (s, 2 H, CH_2); 3.90 (s, 3 H, N—Me); 7.40—7.68 (m, 5 H, arom. H).

***N*,*N*-Dimethyl-*S*-(*p*-nitrobenzyl)thiobenzamidium bromide (1c).** Yield 80%, m.p. 121—123 °C. Found (%): C, 50.06; H, 4.61; N, 7.29; S, 8.46. $C_{16}H_{17}BrN_2O_2S$. Calculated (%): C, 50.40; H, 4.49; N, 7.34; S, 8.41. ^{1}H NMR ($CDCl_3$), δ: 3.47 and 3.83 (both s, 6 H, N—Me); 4.09 (s, 2 H, CH_2); 7.29 (d, 2 H, CH_A, $J_{HA,HB}$ = 8.9 Hz); 7.43—7.62 (m, 5 H, Ph); 7.95 (d, 2 H, 2 CH_B).

***N*,*N*-Dimethyl-*S*-(3-methoxycarbonylallyl)thiobenzimidium bromide (1d).** Yield 75%, m.p. 110—112 °C. Found (%): C, 48.56; H, 5.41; N, 3.92; S, 9.62. $C_{14}H_{18}BrNO_2S$. Calculated (%): C, 48.84; H, 5.27; N, 4.07; S, 9.31. ^{1}H NMR ($CDCl_3$), δ: 3.61 (s, 3 H, N—Me); 3.62 (d, 2 H, CH_2); 3.71 (s, 3 H, O—Me); 3.96 (s, 3 H, N—Me); 5.60 (d, 1 H, CH); 6.61 (dt, 1 H, CH, $J_{CH=CH}$ = 15.4 Hz, J_{CH-CH2} = 7.0 Hz); 7.65—7.77 (m, 5 H, arom. H).

***N*,*N*-Dimethyl-*S*-(2-methyl-3-methoxycarbonylallyl)thiobenzimidium bromide (1e).** Yield 82%, m.p. 118—120 °C. Found (%): C, 49.93; H, 5.56; N, 3.65; S, 8.83. $C_{15}H_{20}BrNO_2S$. Calculated (%): C, 50.28; H, 5.63; N, 3.91; S, 8.95. ^{1}H NMR (DMSO-d_6), δ (a mixture of *E*- and *Z*-isomers): 2.85 and 2.94 (both s, 3 H total, Me); 3.27 and 3.52 (both s, 3 H, N—Me); 3.29 and 3.58 (both s, 3 H, N—Me); 3.66 and 3.69 (both s, 3 H, O—Me); 3.66 and 4.15 (both s, 2 H, CH_2); 5.25 and 5.70 (both s, 1 H, CH); 7.50—7.70 (m, 5 H, arom. H).

3-Dimethylamino-1,3-diphenylprop-2-en-1-one (7). *A.* A solution of Et_3N (1.1 mmol) in MeCN (1 mL) was added with

stirring under argon to a solution of bromide **1a** (1 mmol) in MeCN (3 mL) at ~20 °C. The mixture was stirred for 2 h and concentrated *in vacuo*, and the residue was chromatographed on L 40/100 silica gel (benzene—acetone, 6 : 1). The yield of enaminone **7** was 72%, that of *N,N*-dimethylthiobenzamide was 26%.

B. A mixture of *N,N*-dimethylbenzamide diethyl acetal (0.03 mol) and freshly distilled acetophenone (0.028 mol) was refluxed for 35 h in 15 mL of dry toluene. The solvent was evaporated *in vacuo*, and the residue was distilled; the fraction with b.p. 182—185 °C (0.5 Torr) was collected.[11] Yield 35%. ^{1}H NMR (CD_3OD), δ: 3.01 (s, 6 H, NMe_2); 5.95 (s, 1 H, CH); 7.10—8.05 (m, 10 H, arom. H).

(*E,E*)-Divinyl sulfides (6). A solution of Et_3N (2.2 mmol) in MeCN (2 mL) was added under argon at ~20 °C to a stirred solution of *S*-alkyl-*N,N*-dimethylthiobenzimidium bromide (**6a—e**, 2 mmol) and acetylene derivative (**4a,b**, 2.2 mmol) in MeCN (6 mL). The mixture was stirred for 1 h, and the solvent was evaporated *in vacuo*. The product was crystallized from methanol or isolated by column chromatography.

(*E,E*)-1′-Benzoyl-2′-dimethylamino-1,2-di(methoxycarbonyl)-2′-phenyldivinyl sulfide (6a). Yield 67%, m.p. 146—148 °C (from MeOH). Found (%): C, 65.00; H, 5.61; N, 3.75; S, 7.54. $C_{23}H_{23}NO_5S$. Calculated (%): C, 64.92; H, 5.45; N, 3.29; S, 7.54. MS, *m/z*: 425 $[M]^+$. IR, ν/cm^{-1}: 1705, 1720 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.99 (s, 6 H, N—Me); 3.68 and 3.71 (both s, 6 H, O—Me); 5.64 (s, 1 H, CH); 7.31—7.44 (m, 8 H, arom. H); 7.68 (d, 2 H, arom. H).

(*E,E*)-1,2,1′-Tribenzoyl-2′-dimethylamino-2′-phenyldivinyl sulfide (6b). Yield 62%, m.p. 214—216 °C (from MeOH). Found (%): C, 75.58; H, 5.26; N, 2.68; S, 5.82. $C_{33}H_{27}NO_3S$. Calculated (%): C, 76.57; H, 5.26; N, 2.71; S, 6.20. MS, *m/z*: 517 $[M]^+$. IR, ν/cm^{-1}: 1640, 1570 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.00 (s, 6 H, N—Me); 7.00 (s, 1 H, CH); 7.20—7.82 (m, 15 H, arom. H).

2′-Dimethylamino-1,2,1′-tri(methoxycarbonyl)-2′-phenyldivinyl sulfide (6c). Yield 62%, oil. Found (%): C, 56.82; H, 5.90; N, 3.53; S, 7.85. $C_{18}H_{21}NO_6S$. Calculated (%): C, 56.98; H, 5.58; N, 3.69; S, 8.45. MS, *m/z*: 379 $[M]^+$. IR, ν/cm^{-1}: 1705, 1720 (C=O). ^{1}H NMR ($CDCl_3$), δ: (*E,E*)-isomer: 2.98 (s, 6 H, N—Me); 3.70, 3.77, and 3.80 (all s, 9 H, O—Me); 5.64 (s, 1 H, CH); 7.30—7.50 (m, 5 H, arom. H); (*E,Z*)-isomer: 3.05 (s, 6 H, N—Me); 3.33, 3.77, and 3.91 (all s, 9 H, O—Me); 5.71 (s, 1 H, CH); 7.30—7.50 (m, 5 H, arom. H).

2′-Dimethylamino-1,2-di(methoxycarbonyl)-1′-*p*-nitrophenyl-2′-phenyldivinyl sulfide (6d). Yield 69%, m.p. 155—156 °C (from MeOH). Found (%): C, 59.95; H, 4.97; N, 6.17; S, 7.08. $C_{22}H_{22}N_2O_6S$. Calculated (%): C, 59.72; H, 5.01; N, 6.33; S, 7.25. MS, *m/z*: 442 $[M]^+$. IR, ν/cm^{-1}: 1715 (C=O); 1575 (asymm. NO_2); 1320 (symm. NO_2). ^{1}H NMR ($CDCl_3$), δ: (*E,E*)-isomer: 2.59 (s, 6 H, N—Me); 3.58 and 3.63 (both s, 6 H, O—Me); 5.52 (s, 1 H, CH); 7.10—8.10 (m, 9 H, arom. H); (*E,Z*)-isomer: 2.94 (s, 6 H, N—Me); 3.58 and 3.63 (both s, 6 H, O—Me); 5.58 (s, 1 H, CH); 7.10—8.10 (m, 9 H, arom. H).

2′-Dimethylamino-1,2-di(methoxycarbonyl)-1′-(2-methoxycarbonylvinyl)-2′-phenyldivinyl sulfide (6e). Yield 65%, oil. Found (%): C, 58.89; H, 5.56; N, 3.72; S, 7.51. $C_{20}H_{23}NO_6S$. Calculated (%): C, 59.24; H, 5.72; N, 3.46; S, 7.91. MS, *m/z*: 405 $[M]^+$. IR, ν/cm^{-1}: 1700, 1725 (C=O). ^{1}H NMR ($CDCl_3$), δ: (*E,E*)-isomer: 3.01 (s, 6 H, N—Me); 3.59, 3.68, and 3.90 (all s, 9 H, O—Me); 5.50 (s, 1 H, CH); 5.84 (d, 1 H, CH_A); 5.92 (d, 1 H, CH_B, $J_{HA,HB}$ = 14.8 Hz); 7.35—7.50 (m, 5 H, arom. H); (*E,Z*)-isomer: 3.05 (s, 6 H, N—Me); 3.66, 3.72, and 3.90 (all s, 9 H, O—Me); 5.55 (s, 1 H, CH); 7.00 (d, 1 H, CH_A); 7.75 (d, 1 H, CH_B, $J_{HA,HB}$ = 14.8 Hz); 7.30—7.50 (m, 5 H, arom. H).

2′-Dimethylamino-1,2-di(methoxycarbonyl)-1′-(1-methyl-2-methoxycarbonylvinyl)-2′-phenyldivinyl sulfide (6f). Yield 65%, oil. Found (%): C, 59.78; H, 5.82; N, 3.69; S, 7.31. $C_{21}H_{25}NO_6S$. Calculated (%): C, 60.12; H, 6.01; N, 3.34; S, 7.64. MS, *m/z*: 419 $[M]^+$. IR, ν/cm^{-1}: 1700, 1720 (C=O). ^{1}H NMR ($CDCl_3$), δ: (*E,E*)-isomer: 2.10 (s, 3 H, Me); 2.62 (s, 6 H, N—Me); 3.58, 3.63, and 3.68 (all s, 9 H, O—Me); 5.50 (s, 1 H, CH); 7.20—7.45 (m, 5 H, arom. H); (*E,Z*)-isomer: 2.30 (s, 3 H, Me); 2.73 (s, 6 H, N—Me); 3.62, 3.65, and 3.76 (all s, 9 H, O—Me); 5.72 (s, 1 H, CH); 7.20—7.45 (m, 5 H, arom. H).

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-32095) and the State Committee on Higher Education (Science and Engineering Program "Fine Organic Synthesis", Project FT-12).

References

1. R. M. Kellogg, *Tetrahedron*, 1976, **23**, 2165.
2. L. Xingya and R. Huisgen, *Tetrahedron Lett.*, 1983, **24**, 4181.
3. E. J. Smutny, *J. Am. Chem. Soc.*, 1969, **91**, 1208.
4. T. Suito, H. Agukawa, N. Sumizawa, T. Shizuta, S. Motoki, and K. Kobagashi, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1405.
5. R. Huisgen, C. Fulka, I. Kalwinsch, L. Xingya, G. Mloston, J. R. Morgan, and A. Probstl, *Bull. Soc. Chim. Belg.*, 1984, **93**, 511.
6. I. V. Magedov, V. N. Drozd, S. Yu. Shapakin, and D. S. Yufit, *Sulfur Lett.*, 1994, **17**, 125.
7. K. Hayakawa, Y. Kamikawaji, and K. Kanematsu, *Tetrahedron Lett.*, 1982, **23**, 2171.
8. K. Hayakawa, Y. Kamikawayi, A. Wakita, and K. Kanematsu, *J. Org. Chem.*, 1984, **49**, 1985.
9. A. V. Fokin and A. F. Kolomiets, *Khimiya tiiranov* [*Chemistry of Thiiranes*], Nauka, Moscow, 1978, 343 pp. (in Russian).
10. C. C. Tang and A. J. Speziale, *J. Org. Chem.*, 1964, **29**, 1577.
11. S. S. Tseng, J. W. Epstein, H. J. Brabender, and Y. Francisco, *J. Heterocycl. Chem.*, 1987, **47**, 389.
12. D. Klamann, in Houben-Weyl, *Methoden der Organischen Chemie, Organische Schwefel-Verbindungen*, Georg Thieme Verlag, Stuttgart—New York, 1985, **E11**, 158.
13. D. Klamann, in Houben-Weyl, *Methoden der Organischen Chemie, Organische Schwefel-Verbindungen*, Georg Thieme Verlag, Stuttgart—New York, 1985, **E11**, 1483.
14. R. P. Singh, V. D. Gupta, E. N. Duesler, and C. K. Narula, *J. Chem. Soc., Dalton Trans.*, 1988, 1289.
15. J. Kao, *J. Am. Chem. Soc.*, 1978, **100**, 4685.
16. N. U. Kamath and K. Venkatesan, *Acta Crystallogr.*, 1984, **C40**, 1211.
17. B. Tinant, J.-P. Declercq, M. Vermander, Z. Janousek, and H. G. Viehe, *Acta Crystallogr.*, 1990, **C46**, 1145.

Received November 15, 1996