Reactions of Ketone Hydrazones and β-Keto Enamines with Disulfur Dichloride. New Synthesis of Thioketones and 5*H*-1,2,3-Dithiazoles

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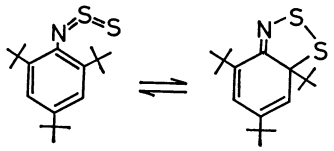
Ketone hydrazones react with disulfur dichloride in the presence of triethylamine to afford thioketones in good yields. The reaction mechanism involving *N*-thiosulfinylamine ($R_2C{=}N{-}N{=}S{=}S$) and *S*-thioxothioketone ($R_2C{=}S{=}S$) is proposed. The formation of di-*t*-butyl and di-1-adamantyl thioketones even at low temperatures has been interpreted as steric congestion alone being not enough to stabilize the corresponding *S*-thioxothioketones. The reaction of β-ketoenamines with disulfur dichloride gives 5*H*-1,2,3-dithiazoles *via* intramolecular cyclization of intermediary *N*-thiosulfinylamines.

We previously reported an interesting ring-chain tautomerism for *N*-thiosulfinylaniline **1a** which was prepared by reaction of disulfur dichloride with the corresponding aniline;[1] **1a** is in equilibrium with **1b** in solution, while only **1b** exists in the solid state.[2] The conversion of **1a** to **1b** can be regarded as intramolecular 1,3-dipolar cycloaddition of the *N*-thiosulfinyl group[3] or electrocyclization of 1,5-dipole.[4]



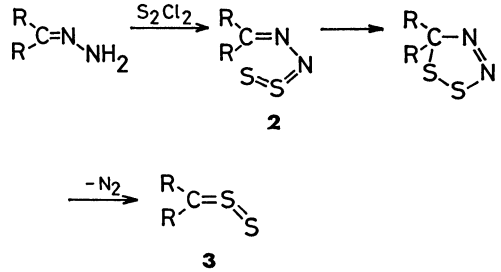
1a **1b**

Such a facile cyclization at the expense of loss of aromaticity observed for **1a** suggests that similar cyclizations are expected to occur also in other systems having X=Y–N=S=S structure.

We report in this paper that the reaction of ketone hydrazones and β-keto enamines with disulfur dichloride indeed proceeds *via* intramolecular cyclization of the *N*-thiosulfinyl group to form thioketones and 5*H*-1,2,3-dithiazoles, respectively.[5]

Results and Discussion

Reactions of Ketone Hydrazones with Disulfur Dichloride. Since a ketone hydrazone is considered to react with disulfur dichloride to give *N*-thiosulfinylamine **2**, which would undergo intramolecular cyclization in view of the tautomerism of **1**, we reasoned that this reaction would provide a route to a hitherto unknown *S*(IV)-thiocumulene, *S*-thioxothioketone **3**.[6]



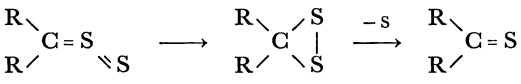
2

3 (1)

The reaction occurred, as expected, smoothly at a low temperature, but the product was not *S*-thioxothioketone but thioketone. For example, simultaneous addition of benzene solutions of di-*t*-butyl ketone hydrazone and disulfur dichloride to a benzene solution of triethylamine at 0 °C afforded di-*t*-butyl thioketone in 96% yield. The formation of di-*t*-butyl thioketone is most probably due to loss of a sulfur atom from the expected thioxothioketone which is unstable at the reaction temperature.

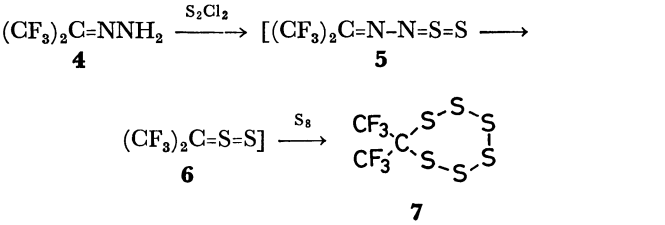
In the hope that the reaction at lower temperatures would enable the isolation of the thioxothioketone, the same reaction was carried out at −85 °C with toluene as solvent, but the product was again di-*t*-butyl thioketone (97%). The reaction using di-1-adamantyl ketone hydrazone in toluene at −90 °C also gave di-1-adamantyl thioketone (pink crystals, 71%). These reactions proceeded very fast, and the color due to the thioketones appeared during the addition of the reagents, suggesting that the thioxothioketone was too unstable to decompose into the thioketone even at such low temperatures.

Decomposition of *S*(IV)-thiocumulenes with loss of sulfur is generally believed[7] to proceed *via* cyclization into a three-membered ring as shown below and, therefore, such a change as from 3-coordinated to 4-coordinated carbon would be less favorable as R group becomes bulkier.



The failure of formation of thioxothioketone having such a bulky group as *t*-butyl or 1-adamantyl suggests that the steric congestion alone is not enough to stabilize the thioxothioketone.

It is known that as the electronegativity of X in thiocumulenes X=S=O or X=S=N–R increases, the S=O bond in the former or the S=N bond in the latter becomes stronger as suggested by shortening of the bond length.[8] If this is the case with the thioxothioketone, then the use of a hydrazone bearing strongly electron-withdrawing substituents is expected to lead to a more stable thiocumulene. To this end, hexafluoroacetone hydrazone (**4**)[9] was allowed to react with disulfur dichloride at −23 °C, but thioxothioketone **6** was not formed, the only characterizable



4 **5** **6** **7**

product being 7,7′-bis(trifluoromethyl)-1,2,3,4,5,6-hexathiacycloheptane (**7**) (3%) along with some sulfur.

A reaction closely related to the above has been reported;[10] *N*,*N*-bis(trimethylsilyl)sulfonamides **8** react with disulfur dichloride to give an eight-membered heterocycle **10**. Since the formation of **10** is explained by the reaction of thiosulfinylamine intermediate **9** with sulfur formed during the reaction,[10] a similar

$$R_2N\text{-}SO_2\text{-}N(SiMe_3)_2 \xrightarrow{S_2Cl_2} [R_2N\text{-}SO_2\text{-}N{=}S{=}S]$$

8 **9**

$$\xrightarrow{S_8} R_2NSO_2\text{-}N\text{(S-S-S-S-S)}$$

10

mechanism *via* **5** and **6** is thought to be operative in the formation of **7**.

An attempt to trap **6** by cycloaddition with dibenzoylacetylene was unsuccessful.[3]

Although the reaction of ketone hydrazones with disulfur dichloride did not give expected *S*-thioxothioketones, the formation of thioketones in good yields indicates that the present reaction provides a simple, new method for the synthesis of thioketones from hydrazones and the results using some hydrazones are listed in Table 1.

Table 1. Synthesis of thioketones from hydrazones ($R^1R^2C{=}NNH_2$)[a]

Hydrazones		Yield/% of thioketones	
R^1	R^2	UV	Isolated
t-Bu	*t*-Bu	Quant.	66
1-Ad[b]	1-Ad	71	59
$-Me_2CCH_2CH_2CMe_2-$[c]		Quant.	58
$C_{10}H_{16}$[d]		Quant.	54
$C_{10}H_{16}$[e]		63	
Ph	Ph	54	

a) The reactions were carried out in benzene at 5 °C except for di-1-adamantyl ketone hydrazone, where the reaction was done in toluene at −90 °C. b) 1-Ad denotes 1-adamantyl. c) 2,2,5,5-Tetramethylcyclopentanone hydrazone. d) Fenchone hydrazone. e) Camphor hydrazone.

The yields for sterically hindered thioketones are usually excellent although isolated yields are somewhat diminished. The simultaneous addition of the both substrates has to be done to get a good yield of thioketones. For example, the simultaneous addition method gave thiobenzophenone in 54% yield while the addition of a benzene solution of a hydrazone and triethylamine to disulfur dichloride in benzene formed the thioketone in 8%; the yield was 37% when the reverse addition was used.

The solvent effect of this reaction is remarkable. Although the reactions of di-*t*-butyl ketone hydrazone with disulfur dichloride in benzene and toluene gave di-*t*-butyl thioketone in 96 and 97% respectively as previously described, those in dichloromethane and ether resulted in the yields of 39 and 37% respectively. Thus, the aromatic hydrocarbon is a solvent of choice in the present reaction.

Another preparative method of thioketones from hydrazones, which uses the reaction of phosphoranes with sulfur, has recently been reported,[11] but we believe that the present method is simpler in manipulation and the reaction conditions are milder.

Although the pathway *via* thioxothioketone (Eq. 1) is considered to be a most likely mechanism for the formation of thioketones, other two mechanisms are also conceivable. One is oxidation of a hydrazone with disulfur dichloride to give a diazomethane, followed by the reaction with sulfur (Eq. 2)[12] and the other involves loss of the terminal sulfur from *N*-thiosulfinylamine intermediate to give thionitroso compound **11** followed by cyclization and loss of nitrogen molecule (Eq. 3).

$$R_2C{=}NNH_2 \xrightarrow{S_2Cl_2} R_2C{=}\overset{+}{N}{=}\overset{-}{N} \xrightarrow[-N_2]{S_8} R_2C{=}S \qquad (2)$$

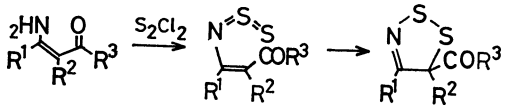
$$R_2C{=}NNH_2 \xrightarrow{S_2Cl_2} R_2C{=}N\text{-}N{=}S{=}S \xrightarrow{-S} R_2C{=}N\text{-}N{=}S$$

11

$$\longrightarrow \begin{matrix} R_2C\text{—}N \\ | \quad \| \\ S\text{—}N \end{matrix} \xrightarrow{-N_2} R_2C{=}S \qquad (3)$$

The possibility of Eq. 2 was eliminated by the fact that the reaction of diphenyldiazomethane with sulfur in the presence of triethylamine did not give thiobenzophenone under identical conditions. No di-*t*-butyl thioketone was formed by the reaction of di-*t*-butyl ketone hydrazone with sulfur dichloride (SCl_2) in the presence of triethylamine which is expected to yield **11** (R=*t*-Bu), thus ruling out the possibility of Eq. 3.

Reaction of β-Keto Enamines with Disulfur Dichloride. Since β-keto enamines **12** are known to exist as enamine form instead of imine form,[13] the reaction of β-ketoenamines with disulfur dichloride is expected to lead to *N*-thiosulfinylamine **13** or its cyclized form, 5*H*-1,2,3-dithiazole **14** (Eq. 4).



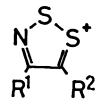
(4)

12 **13** **14**

a: $R^1R^2=(CH_2)_4$, R^3=OEt
b: $R^1R^2=(CH_2)_3$, R^3=OEt
c: $R^1=R^3$=Me, R^2=H
d: R^1=Me, R^2=H, R^3=OEt
e: $R^1=R^2=R^3$=Me
f: R^1=Ph, $R^2=R^3$=Me
g: $R^1=R^2$=Me, R^3=OEt

The reaction indeed proceeded as expected. 1-Amino-2-ethoxycarbonyl-1-cyclohexene (**12a**) was allowed to react with disulfur dichloride to give 6-ethoxycarbonyl-7,8-dithia-9-azabicyclo[4.3.0]non-1(9)-ene (**14a**) in 74% yield. The product was a stable yellow liquid and identified by spectral and analytical data. The electronic spectrum (λ_{max} 380 nm, ε 290) clearly inidicates that the product is not *N*-thiosulfinylamine **13** but 5*H*-1,2,3-dithiazole **14**; the *N*-thio-

sulfinylamine should have a strong absorption in the visible region (*e.g.*, 538 nm (ε 39000) for *p*-(dimethylamino)-*N*-thiosulfinylaniline[3] and 584 nm (ε 1280) for 2,4-di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline).[1] The mass spectrum showing the fragment of M^+-CO_2Et as a strong base peak is also in keeping with the structure **14**, since cation **15** is a stable 6π-aromatic system and hence is easily formed. The strong peak of M^+-

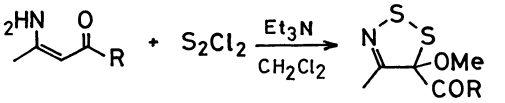


15

COR^3 (*i.e.* **15**) is characteristic of all the products **14 a,c′,d′,e,f** obtained in this study (see Experimental).

Contrary to the successful isolation of **14a**, the reaction of 1-amino-2-ethoxycarbonyl-1-cyclopentene **12b** with disulfur dichloride resulted in black polymeric products. In this case intermediary **13b** is unable to cyclize into **14b** probably because of strain due to two fused five-membered rings and polymerizes *via* intermolecular reaction. Since attempts to prepare 1-amino-2-ethoxycarbonyl-1-cycloheptene, 1-amino-2-ethoxycarbonyl-1-cyclooctene and 1-amino-2-ethoxycarbonyl-1-cyclododecene by the same procedure[13] as used for **12a** and **12b** were unsuccessful, the effect of a ring size on the stability of **14** ($R^1R^2=(CH_2)_n$) could not be studied.

The reaction of 4-amino-3-penten-2-one (**12c**) with disulfur dichloride in the presence of triethylamine at 0 °C in dichloromethane give a trace amount (0.75%) of 5-acetyl-5-methoxy-4-methyl-5*H*-1,2,3-dithiazole (**14c′**) instead of **14c** as a sole isolable product. Since the methoxyl group in **14c′** was thought to come from

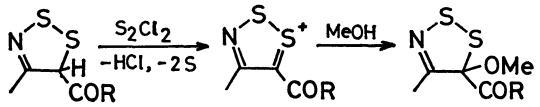


12c: R=Me **14c′**: R=Me
12d: R=OEt **14d′**: R=OEt

methanol present in dichloromethane as stabilizer, the reaction using an equimolar amount of methanol and two molar equivalents of disulfur dichloride and triethylamine was carried out to give 53% of **14c′**.

A similar reaction of ethyl 3-amino-2-butenoate (**12d**) with disulfur dichloride in the presence of triethylamine and methanol gave 35% of 5-ethoxycarbonyl-5-methoxy-4-methyl-5*H*-1,2,3-dithiazole (**14d′**) (R=OEt). The reaction without methanol under otherwise identical conditions gave no product other than sulfur.

The formation of **14c′,d′** can be explained in terms of oxidation of the hydrogen at 5-position in intermediary **14c,d** by disulfur dichloride followed by reaction of methanol with a resulting dithiazolium ion **15**. The relation of this reaction with the Herz reaction[14]



14c,d **15** **14c′,d′**

Table 2. Synthesis of 5*H*-1,2,3-dithiazoles

Dithiazoles	Yield/%	Bp (°C, mmHg**)	Mp/°C
14a	73	115, 0.5	
14c′	53	136, 5	
14d′	35	100, 6	
14e	83	83, 6	
14f	6.4	110, 6	68—69

** 1 mmHg=133.322 Pa.

has already been discussed.[5b]

In support of the above mechanism, the reaction of 4-amino-3-methyl-3-penten-2-one (**12e**) where there is no hydrogen to be oxidized gave 5-acetyl-4,5-dimethyl-5*H*-1,2,3-dithiazole (**14e**) in 83% yield. A similar reaction also took place with 4-amino-3-methyl-4-phenyl-3-buten-2-one (**12f**) to afford 5-acetyl-5-methyl-4-phenyl-5*H*-1,2,3-dithiazole (**14f**) in 6.4% yield. Although 3-amino-2-methyl-2-butenoate (**12g**) was allowed to react under the same conditions, only polymeric products were obtained for reasons unclear to us yet.

The dithiazoles **14** are thought to be produced by the intramolecular cycloaddition of thiosulfinylamino group to the carbon-carbon double bond of **13**. This is the first synthesis of the compound with a 5*H*-1,2,3-dithiazole ring in the aliphatic system. The 5*H*-1,2,3-dithiazoles synthesized in the present study are summarized in Table 2.

The spectral data indicate that there is no equilibrium between **13** and **14** in the case of these dithiazoles in contrast to the system **1a**⇌**1b**. The visible spectra do not show any absorption due to *N*-thiosulfinyl group (–N=S=S) as mentioned previously. Any peak assignable to the open-chain structure **13** was not observed also in the NMR spectra. However, there still remains a possibility that **14** exists as an equilibrium mixture with **13** to such an extent that it cannot be detected spectroscopically. To check this possibility, the reactions of **14e** with some dipolarofiles (norbornadienes, *N*-phenylmaleimide, 4-phenyl-1,2,4-triazole-3,5-dione, dimethyl acetylenedicarboxylate) were carried out under various conditions,[3] but the cycloadducts were not obtained. These facts seem to suggest that **14** does not dissociate into **13** to an appreciable extent.

Experimental

NMR spectra were recorded at 60 MHz in deuteriochloroform on a Hitachi R-24B or a Hitachi R-24 spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi RMU-6L mass spectrometer. High resolution mass spectra were obtained with a JOEL D-300 mass spectrometer. Infrared spectra were recorded on a Hitachi EPI-G2 or a Hitachi 260-30 infrared spectrophotometer. Ultraviolet and visible spectra were taken on a Hitachi EPS-3 spectrophotometer or a Hitachi 340 recording spectrophotometer. All melting points were uncorrected. The reactions of hydrazones and enamines with disulfur dichloride were carried out under argon atmosphere.

Materials. Disulfur dichloride was distilled from sul-

fur and active carbon and stored in ampules in a refrigerator. Di-*t*-butyl ketone and di-1-adamantyl ketone hydrazones were prepared by the reported method.[15] The hydrazones of camphor, fenchone, 2,2,5,5-tetramethylcyclopentanone and benzophenone were prepared from the corresponding ketones by the method of Barton.[16] 2,2,5,5-Tetramethylcyclopentanone was prepared by the exaustive methylation of cyclopentanone.[17] Hexafluoroacetone hydrazone[9] was prepared from hexafluoroacetone. β-Ketoenamines were prepared from the corresponding β-diketones by the method of Kloek and Leshinsky,[18] and the new enamines **12 e,f,g** had following properties. **12e**: mp 118 °C; NMR ($CDCl_3$): δ=1.83 (3H, s), 1.95 (3H, s), 2.13 (3H, s), and 6.8—8.0 (2H, broad); IR (KBr): 3250, 3100, 1600, 1500—1420, 1280, 1220, 970, and 650 cm^{-1}; MS: *m/e* (rel intensity) 113 (M^+, 76), 98 (100), 70 (44), 55 (20), and 43 (38). Found: C, 63.54; H, 10.09; N, 12.25%. Calcd for $C_6H_{11}NO$: C, 63.69; H, 9.80; N, 12.38%. **12f**: mp 146.5—147.0 °C; NMR ($CDCl_3$): δ=1.66 (3H, s), 2.08 (3H, s), and 7.12 (s), 6.5—9.0 (broad) (7H in total); IR (KBr): 3250, 3100, 1600, 1500—1420, 1300, 1000, and 700 cm^{-1}; MS: *m/e* (rel intensity) 175 (M^+, 42), 174 (100), 160 (8), 105 (23), 98 (32), and 77 (31). Found: C, 75.28; H, 7.52; N, 7.72%. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99%. **12g**: mp 51.0—51.5 °C; NMR ($CDCl_3$): δ=1.23 (3H, t, J=7 Hz), 1.78 (3H, d, J=11 Hz), 4.03 (2H, q, J=7 Hz), and 5.5—7.0 (2H, broad); IR (KBr): 3370, 3120, 1600, 1500, 1270, 1220, 970, and 650 cm^{-1}. Found: C, 58.33; H, 9.16; N, 9.30%. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78%.

Reaction of Di-t-butyl Ketone Hydrazone with Disulfur Dichloride. a) In Benzene: To an ice-cold solution of triethylamine (1.06 g, 10.5 mmol) in benzene (20 cm^3) were added simultaneously benzene solutions (10 cm^3 each) of di-*t*-butyl ketone hydrazone (0.78 g, 5 mmol) and disulfur dichloride (0.71 g, 5.25 mmol) at about the same rate using two dropping funnels during 15 min. After stirring for 30 min at room temperature, the reaction mixture was washed with water and dried over anhydrous magnesium sulfate. The yield determined for the solution by the visible spectrum (λ_{max}(ethanol) 536 nm (ε 8.9))[18] was 96%. After removal of the solvent under reduced pressure, the residue was subjected to bulb to bulb distillation (bp 90—116 °C, 18 mmHg**) to give 521 mg (66%) of pure di-*t*-butyl thioketone as pink oil.[16]

b) In Other Solvents: Similar reactions in toluene (−85 °C), ether (−100 °C), dichloromethane (−90 °C) using 3 mmol of the hydrazone afforded the thione in 97, 37, and 39% (estimated by the visible spectra), respectively.

Reaction of Di-t-butyl Ketone Hydrazone with Sulfur Dichloride. To an ice-cold benzene solution (20 cm^3) of triethylamine (1.687 g, 16.7 mmol) were added simultaneously benzene solutions (15 cm^3 each) of di-*t*-butyl ketone hydrazone (1.241 g, 7.95 mmol) and sulfur dichloride (0.86 g, 8.35 mmol). After stirring for 1 h at room temperature, the deep red reaction mixture was washed with water and dried over anhydrous magnesium sulfate. The visible spectrum showed the absence of di-*t*-butyl thioketone. TLC of the reaction mixture also showed that di-*t*-butyl thioketone was not produced in this reaction. Removal of the solvent gave 1.267 g of red oil, 761 mg of which was subjected to bulb to bult distillation to give 251 mg (20%, based on the hydrazone) of di-*t*-butyl thioketone and 43 mg of unidentifiable yellow oil. This suggested that the thione was formed by the thermal decomposition of the reaction mixture.

Reaction of Di-1-adamantyl Ketone Hydrazone with Disulfur Dichloride. The reaction of the hydrazone (330 mg, 1.06 mmol) using the above simultaneous addition method was carried out at −85 °C, and the yield was determined for the reaction solution by the visible spectrum to be 71%. After removal of the solvent under reduced pressure, the residue was purified by TLC (silica gel, hexane) to give 195 mg (59%) of di-1-adamatyl thioketone as pink crystals: mp 184.5—185.0 °C; NMR ($CDCl_3$): δ=1.60—1.80 (18H, m) and 2.00—2.30 (12H, m); IR (KBr): 2950, 1730, 1610, 1440, 1290, 1220, 1140, 1100, 1020, and 720 cm^{-1}; MS *m/e* (rel intensity) 314 (M^+, 13), 179 (17), and 135 (100); UV: λ_{max} (benzene) 548 nm (ε 16.6), λ_{max} (hexane) 548 nm (ε 13.9); Found: C, 80.47; H, 9.35; S, 10.11%. Calcd for $C_{21}H_{30}S$: C, 80.19; H, 9.61; S, 10.19%.

Reaction of Other Hydrazones with Disulfur Dichloride. a) 2,2,5,5-Tetramethylcyclopentanone and Fenchone Hydrazones: The cyclopentanone (155 mg, 1.0 mmol) and fenchone hydrazones were allowed to react with disulfur dichloride in benzene at 5 °C by a method similar to that described for di-*t*-butyl ketone hydrazone (the simultaneous addition method). The yield was determined for the reaction mixture to be quantitative for both the thiones using the literature values of n-π^* absorption.[19,20] After removal of the solvent, the residue was subjected to bulb to bulb distillation to give pure thiones: the cyclopentane thione, 92 mg (58%), bp 116 °C (121 mmHg);[18] thiofenchone, 457 mg (54%), bp 120 °C (10 mmHg).[20]

b) Camphor and Benzophenone Hydrazones: The reactions of the two hydrazones were carried out by the simultaneous addition method in benzene at 5 °C. The reaction mixtures were analyzed for the corresponding thiones by the electronic spectra (n-π^* band), the yields of thiocamphor[19] and thiobenzophenone[20] being 63 and 54%, respectively. The addition of a solution of the benzophenone hydrazone and triethylamine to that of disulfur dichloride and the addition of a solution of disulfur dichloride to that of the hydrazone and triethylamine gave thiobenzophenone in 8 and 37% yields, respectively, as estimated by the electronic spectra.

Reaction of Hexafluoroacetone Hydrazone with Disulfur Dichloride. To a dichloromethane solution (30 cm^3) of triethylamine (5.34 g, 52.9 mmol) cooled with carbon tetrachloride–Dry Ice bath at −23 °C, were added simultaneously dichloromethane solutions (10 cm^3 each) of hexafluoroacetone hydrazone (5 g, 27.8 mmol) and disulfur dichloride (3.75 g, 26.5 mmol) during 1 h. After stirring for 30 min at room temperature, precipitated triethylamine hydrochloride was filtered off, the filtrate was passed through a short column of silica gel, and the solvent was removed under reduced pressure to give 4.12 g of a red-purple oil. Bulb to bult distillation (bp 110 °C, 0.5 mmHg) of the oil gave 1.15 g of a red oil, which was subjected to chromatographic separation (TLC, silica gel, carbon disulfide) to afford 254 mg (2.7%) of **7**: bp 110 °C (0.5 mmHg); IR (neat): 1280—1140, 925, 880, 840, 730, and 700 cm^{-1}; Found: *m/e* 341.8250. Calcd for $C_3F_6S_6$: M, 341.8228. MS: *m/e* (rel intensity) 342 (M^+, 34), 278 (100), 259 (9), 246 (3), 227 (2), 214 (60), and 182 (21).

*Reactions of β-Ketoenamines with Disulfur Dichloride. a) 1-Amino-2-ethoxycarbonyl-1-cyclohexene (**12a**)*: To a solution of **12a** (200 mg, 1.18 mmol) and triethylamine (2.51 mg, 2.49 mmol) in dichloromethane (20 cm^3) was added dropwise a solution of disulfur dichloride (168 mg, 1.24 mmol) in dichloromethane (10 cm^3) at room temperature during 30 min. After additional stirring at room temperature for 1 h, the reaction mixture was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left 271 mg of orange oil, which

**1 mmHg=133.322 Pa.

was purified by TLC (silica gel, dichloromethane) to give **14a** (203 mg, 74%) as yellow oil: bp 115 °C (0.5 mmHg); NMR ($CDCl_3$): δ=1.25 (t, J=7 Hz) and 1.0—3.1 (m) (11H in total), and 4.16 (2H, q, J=7 Hz); IR (neat): 2950, 1730, 1610, 1440, 1290, 1220, 1140, 1100, 1020, and 720 cm^{-1}; MS: *m/e* (rel intensity) 231 (M^+, 17) and 158 (100); UV: λ_{max} (hexane): 380 (ε 288), 278 (1890), and 234 nm (2010). Found: C, 46.48; H, 5.64; N, 5.92; S, 27.28%. Calcd for $C_9H_{13}O_2NS_2$: C, 46.73; H, 5.66; N, 6.05; S, 27.72%.

*b) 1-Amino-2-ethoxycarbonyl-1-cyclopentene (**12b**)*: To an ice-cold solution of **12b** (298 mg, 1.92 mmol) and triethylamine (427 mg, 4.23 mmol) in dichloromethane (20 cm^3) was added a solution of disulfur dichloride (286 mg, 2.11 mmol) in dichloromethane (10 cm^3) dropwise during 30 min. The color of the solution turned from yellow to black-brown at the end of the addition. Treatment of the reaction mixture gave no identifiable product.

*c) 4-Amino-3-penten-2-one (**12c**)*: The reaction of **12c** (1.043 g, 10.5 mmol) was carried out at 0 °C by the procedure described in *a)*. Chromatographic separation (DCC, silica gel, CCl_4) and Kugel Rohr distillation (bp 60 °C, 5 mmHg) gave 15 mg (0.75%) of **14c′** as yellow oil: NMR ($CDCl_3$): δ=2.05 (3H, s), 2.32 (3H, s), and 3.18 (3H, s); IR (neat): 3450, 3000—2900, 1720, 1430, 1360, 1080, 820 and 740 cm^{-1}; MS: *m/e* (rel intensity) 191 (M^+, 5), 160 (3), and 148 (100); UV: λ_{max}(hexane) 360 (ε 271), 282 (3210), and 244 nm (2710). Found: C, 37.42; H, 4.70; N, 7.49; S, 33.42%. Calcd for $C_6H_9NO_2S_2$: C, 37.68; H, 4.74; N, 7.32; S, 33.52%.

When a dichloromethane solution (10 cm^3) of disulfur dichloride (911 mg, 6.75 mmol) was added to an ice-cold dichloromethane solution (20 cm^3) of **12c** (318 mg, 3.21 mmol), triethylamine (1.36 g, 13.5 mmol), and methanol (0.1 g, 3.21 mmol), 326 mg (53%) of **14c′** was obtained after a similar work up to the above.

*d) Ethyl 3-Amino-2-butenecarboxylate (**12d**)*: A similar reaction with **12d** (372 mg, 2.89 mmol) to that in *c)* in the presence of methanol (92 mg, 2.89 mmol) gave a brown reaction mixture. After washing with water and removal of the solvent, it gave black-brown oil (555 mg), which was subjected to chromatographic separation (DCC, silica gel, dichloromethane–carbon tetrachloride 1:1) to give **14d′** (221 mg, 35%) as brown oil. It was purified by distillation (bp 110 °C, 3 mmHg) to give 194 mg of yellow oil: NMR ($CDCl_3$): δ=1.30 (3H, t, J=7 Hz), 2.15 (3H, s), 3.18 (3H, s), and 4.22 (2H, q, J=7 Hz); IR (neat): 3000—2900, 1740, 1440, 1260, 1100, and 740 cm^{-1}; MS: *m/e* (rel intensity) 221 (M^+, 9), 172 (31), 162 (38), 148 (100), 127 (64), and 126 (81); UV: λ_{max}(hexane) 352 (ε 273), 275 (2930), and 202 nm (3620). Found: C, 38.18; H, 4.85; N, 6.29; S, 29.65%. Calcd for $C_7H_{11}NO_3S_2$: C, 37.99; H, 5.01; N, 6.33; S, 28.98%.

*e) 4-Amino-3-methyl-3-penten-2-one (**12e**)*: The reaction of **12e** (3.56 g, 31.5 mmol) was carried out by the method described in *a)*. After usual work up, purification by Kugel Rohr distillation (bp 83 °C, 6 mmHg) afforded **14e** (4.59 g, 83%) as yellow oil: NMR ($CDCl_3$): δ=1.77 (3H, s), 2.05 (3H, s), and 2.41 (3H, s); IR (neat): 2980, 2930, 1710, 1600, 1430, 1360, 1190, 1090, 960, and 730 cm^{-1}; MS: *m/e* (rel intensity) 175 (M^+, 14), 132 (100), 91 (4), 74 (15), 59 (39), and 43 (68); UV: λ_{max}(hexane) 390 (ε 376), 352 (338), 280 (1530), and 236 nm (1980). Found: C, 41.39; H, 5.26; N, 8.11; S, 36.22%. Calcd for $C_6H_9NOS_2$: C, 41.12; H, 5.18; N, 7.99; S, 36.58%.

*f) 4-Amino-3-methyl-4-phenyl-3-buten-2-one (**12f**)*: The yellow reaction mixture obtained from the reaction of **12f** (300 mg, 1.71 mmol) by the procedure described in *a)* was, after usual work up, subjected to Kugel Rohr distillation to give **14f** (30 mg, 6.4%) as yellow oil which solidified upon standing: bp 110 °C (6 mmHg); mp 68—69 °C; NMR ($CDCl_3$): δ=1.82 (3H, s), 2.37 (3H, s), and 6.9—7.4 (5H, m); IR (KBr): 1705, 1370, 1350, 1200, and 690 cm^{-1}; MS: *m/e* (rel intensity) 237 (M^+, 9), 194 (100), 136 (13), 104 (15), 91 (46), 77 (17), 59 (26), and 43 (32): UV: λ_{max}(hexane) 408 (ε 2340), 348 (2450) 310 (3300), and 246 nm (9120). Found: C, 55.35; H, 4.46; N, 5.69%. Calcd for $C_{11}H_{11}NOS_2$: C, 55.67; H, 4.67; N, 5.70%.

*g) Ethyl 3-Amino-2-methyl-2-butenoate (**12g**)*: The reaction of **12g** (515 mg, 3.60 mmol) by the method described above gave a brown reaction mixture, the usual work up of which afforded no characterizable product.

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