corded on a Varian MAT 311 spectrometer. Column chromatography was carried out on silica gel (Merck Art. 9385, Kieselgel 60). Melting points were determined on an RCH (C. Reichert) microscope with a Kofler heating stage.

General Procedure for the Preparation of 6*H*-1,3-Thiazines 3a and 3b. A mixture of **1a** or **1b** (4.85 mmol) in 30 mL of benzene and 3 mL of freshly distilled methyl vinyl ketone was heated at 140 °C (autoclave) for 5 h with stirring. The thiazine obtained was purified on a silica gel column (elutant, 80/20 petroleum ether/ethyl acetate; yield, 98%). Cycloreversion of **2** to **3a** was carried out with an identical procedure to the previous one, **1a** being replaced by **2** (yield, 98%).

5-Acetyl-2-phenyl-6*H*-1,3-thiazine (3a): ^{1}H and ^{13}C NMR spectra were in agreement with data given in the literature.[13]

5-Acetyl-4-methyl-2-phenyl-6*H*-1,3-thiazine (3b): mp 75–77 °C; ^{1}H NMR ($CDCl_3$) δ 2.4 (6 H, s, CH_3, $COCH_3$), 3.61 (2 H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ 25.1 (t, C^6, $J_{^{13}C-H}$ = 145 Hz), 113.6 (s, C^5), 154 (s, C^4), 164.9 (s, C^2). Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; S, 13.86. Found: C, 67.93; H, 5.63; S, 13.94.

5-Acetyl-4-(ethoxycarbonyl)-2-phenyl-6*H*-1,3-thiazine (3c). To a solution of 1.14 g (4.3 mmol) of **1c** in 30 mL of CH_2Cl_2 were added at 0 °C 2 mL of methyl vinyl ketone and 0.4 g (3 mmol) of $AlCl_3$. Stirring of the reaction mixture was continued at 0 °C for 3 h and then at room temperature for 12 h. After hydrolysis (40 mL of H_2O) and decanting off the aqueous phase the thiazine was purified on a column of silica gel (elutant, 80/20 petroleum ether/ethyl acetate; crystallization from ethanol): mp 66–67 °C; yield 80%; ^{1}H NMR ($CDCl_3$) δ 1.37 (3 H, t, CH_3), 2.42 (3 H, s, $COCH_3$), 3.69 (2 H, s, CH_2), 4.38 (2 H, q, CH_2); ^{13}C NMR ($CDCl_3$) δ 24.5 (t, C^6, $J_{^{13}C-H}$ = 144 Hz), 118.6 (s, C^5), 144 (s, C^4), 165.8 and 167 (2 s, $C^{4'}$ and C^2), 198.3 (s, $C^{5'}$). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.22; S, 11.08. Found: C, 62.00; H, 5.22; S, 10.96.

General Procedure for the Preparation of 4-(Dimethylamino)-2-phenyl-4*H*-1,3-thiazines. 1 (5 mmol) was added at room temperature to the acetylenic compound (5 mmol) in 20 mL of CH_2Cl_2, and the reaction was followed by TLC. The 4*H*-1,3-thiazine was purified on a silica gel column (elutant; 60/40 petroleum ether/ethylacetate, crystallization from methanol).

4-(Dimethylamino)-5,6-bis(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5a): mp 90 °C; yield 81%; ^{1}H NMR ($CDCl_3$) δ 2.45 (6 H, s, NCH_3), 3.88 (6 H, s, OCH_3), 5.80 (H, s, CH); mass spectrum, *m/z* 334 (M^+), MIKE *m/z* 231, 199, CID MIKE *m/z* 231, 216, 199, 188, 184, 172, 155, 141, 129, 113, 104, 98, 88, 84, 73, 60, 47, 44. Anal. Calcd for $C_{16}H_{18}N_2O_4S$: C, 57.46; H, 5.42; N, 8.37; S, 9.59. Found: C, 57.31; H, 5.45; N, 8.36; S, 9.33.

4-(Dimethylamino)-5,6-bis(methoxycarbonyl)-4-methyl-2-phenyl-4*H*-1,3-thiazine (5b): mp 101–102 °C; yield 81%; ^{1}H NMR ($CDCl_3$) δ 1.60 (3 H, s, CH_3), 2.40 (6 H, s, NCH_3), 3.88 (6 H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 80 (s, C^4), 151 (s, C^2). Anal. Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.78; N, 8.04; S, 9.20. Found: C, 58.45; H, 5.83; N, 8.09; S, 9.00.

4-(Dimethylamino)-4-(ethoxycarbonyl)-5,6-bis(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5c): mp 83–84 °C; yield 91%; ^{1}H NMR ($CDCl_3$) δ 1.27 (3 H, t, CH_3), 2.48 (6 H, s, NCH_3), 3.90 (6 H, s, OCH_3), 4.27 (2 H, q, CH_2); ^{13}C NMR ($CDCl_3$) δ 85.4 (s, C^4). Anal. Calcd for $C_{19}H_{22}N_2O_6S$: C, 56.14; H, 5.45; S, 7.89. Found: C, 56.14; H, 5.47; S, 7.99.

4-(Dimethylamino)-5-(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5d): mp 75–77 °C; yield 80%; ^{1}H NMR ($CDCl_3$) δ 2.45 (6 H, s, NCH_3), 3.84 (3 H, s, OCH_3), 6.02 (H^4, s, CH), 7.93 (H^6, s, CH); ^{13}C NMR ($CDCl_3$) δ 72.2 (d, C^4, $J_{^{13}C-H}$ = 160 Hz), 116.6 (s, C^5), 132 (d, C^6, $J_{^{13}C-H}$ = 160 Hz), 154.3 (s, C^2), 164 (s, $C^{5'}$). Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.83; N, 10.14; S, 11.60. Found: C, 60.90; H, 5.99; N, 10.02; S, 11.57.

3-(Dimethylamino)-1,2-bis(methoxycarbonyl)-2-propene-1-thione (6a). **5a** (3 mmol) was heated for an hour in 30 mL of CH_2Cl_2. The reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from ethanol): mp 135 °C; yield 83%; ^{1}H NMR ($CDCl_3$) δ 3.13 (3 H, s, NCH_3), 3.50 (3 H, s, NCH_3), 3.73 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 8.24 (H, s, CH); ^{13}C NMR ($CDCl_3$) δ 114.0 (s, C^2), 162.1 (d, C^3, $J_{^{13}C-H}$ = 176 Hz), 206.3 (s, C^1); mass spectrum, *m/z* 231 (M^+), MIKE *m/z* 231, 199, CID MIKE *m/z* 231, 216, 199, 188, 172, 155, 141, 129, 113, 104, 98, 88, 84, 73, 60, 47, 44. Anal. Calcd for $C_9H_{13}NO_4S$: C, 46.73; H, 5.66; N, 6.05; S, 13.86. Found: C, 46.81; H, 5.63; N, 5.83;, S, 13.65.

4-(Dimethylamino)-2,3,5,6-tetrakis(methoxycarbonyl)-4*H*-thiopyran (7). A mixture of 1 g (4.3 mmol) of **6a** and 610 mg (4.3 mmol) of **4a** in 30 mL of CH_2Cl_2 was heated at reflux for 48 h. After evaporation of the solvent, the reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from ethanol): mp 92–93 °C; yield 83%; ^{1}H NMR ($CDCl_3$) δ 2.28 (6 H, s, $(CH_3)_2$), 3.81 (6 H, s, OCH_3), 3.84 (6 H, s, OCH_3), 5.00 (H^4, s, CH); ^{13}C NMR ($CDCl_3$) δ 59.7 (d, C^4, $J_{^{13}C-H}$ = 150 Hz), 125.9 (s, C^3–C^5), 133 (s, C^2–C^6). Anal. Calcd for $C_{15}H_{19}NO_8S$: C, 48.24; H, 5.13; N, 3.75; S, 8.58. Found: C, 48.24; H, 5.08; N, 3.66; S, 8.59.

3-Acetyl-5-(methoxycarbonyl)-2*H*-thiopyran (8). A mixture of 500 mg (1.8 mmol) of **5d** and 3 mL of methyl vinyl ketone was heated at reflux for 3 h. After evaporation of the excess methyl vinyl ketone, the reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from 90/10 petroleum ether/ethanol): mp 35 °C; yield 98%; ^{1}H NMR ($CDCl_3$) δ 2.45 (3 H, s, $COCH_3$), 3.66 (2 H, s, CH_2), 3.84 (3 H, s, OCH_3), 7.50 and 8.00 (H^4 and H^6, $J_{H^4-H^6}$ = 0.50 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7 (t, C^2, $J_{^{13}C-H}$ = 146 Hz), 122.5 and 124.6 (2 s, C^3 and C^5), 132.9 and 145.8 (C^4, $J_{^{13}C-H}$ = 163 Hz and C^6, $J_{^{13}C-H}$ = 178 Hz). Anal. Calcd for $C_9H_{10}O_3S$: C, 54.52; H. 5.08; S, 16.17. Found: C, 54.40; H, 5.05; S, 15.52.

Registry No. **1a**, 52421-65-5; **1b**, 67229-59-8; **1c**, 87108-97-2; **2a**, 72856-29-2; **3a**, 72856-35-0; **3b**, 95482-64-7; **3c**, 87109-03-3; **4a**, 762-42-5; **4b**, 922-67-8; **5a**, 95482-65-8; **5b**, 95482-66-9; **5c**, 95482-67-0; **5d**, 95482-68-1; **6a**, 95482-69-2; **7**, 95512-41-7; **8**, 95482-70-5; CH_2=$CHCOCH_3$, 78-94-4.

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Reaction of β-Nitroenamines with Electrophilic Reagents. Synthesis of β-Substituted β-Nitroenamines and 2-Imino-5-nitro-4-thiazolines

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β-Nitroenamines are useful synthetic intermediates, and their reactivity is of interest in connection with that of β-aminoenones. The reaction of β-nitroenamines with carbon nucleophiles has been studied extensively.[1–8] In contrast, the reaction of primary and secondary β-nitroenamines with electrophiles has been little studied.[9–11] In a previous paper, we reported a convenient synthesis of the primary and secondary β-nitroenamines (1) from nitroacetone and ammonia and/or primary amines using titanium(IV) chloride as a catalyst.[12] In this paper, we

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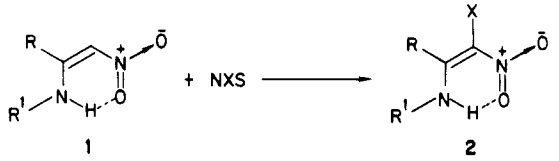
Table I. Reaction of β-Nitroenamines 1 with Thiocyanogen

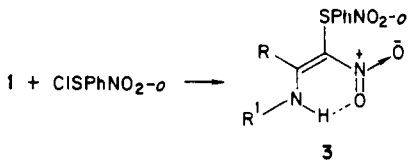
1	reacn temp, °C	reacn time, h	product 4	yield, %	mp, °C	5 or 6	yield, %	mp, °C
1a	0	1.5	4a	50	149–150	5a	0	
1a	room temp	4	4a	0		5a	90	219–220[a]
1b	0	1.5	4b	81	129–130	6b	0	
1b	room temp	2	4b	0		6b	83	148–149
1c	0	1.5	4c	0		6c	73	118–119
1d	0	1.5	4d	0		6d	61	141–142
1f	0	1.5	4f	75	155–156	5f	14	259–260[b]
1f	room temp	2	4f	0		5f	91	259–260
1g	0	1.5	4g	0		6g	81	111–112
1h	0	1.5	4h	58	112–113	6h	19	146–147
1h	room temp	2	4h	0		6h	78	146–147
1i	0	1.5	4i	0		6i	47	195
1j	0	2	4j	75	145–146			

[a] Lit.[13] mp 220 °C. [b] Lit.[14] mp 260 °C.

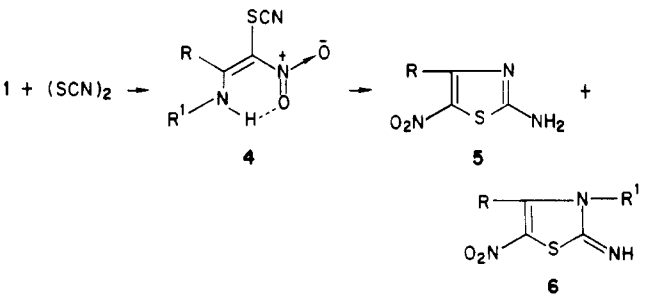
Scheme I



Scheme II



Scheme III



describe the results of the reaction of 1 with some electrophiles—*N*-halosuccinimides (NXS), *o*-nitrobenzenesulfenyl chloride, and thiocyanogen.

Results and Discussion

The reaction of 1 with a small excess of NXS in the dark under a nitrogen atmosphere gave the corresponding β-halo-β-nitroenamines, **2a–4** (X = Cl, Br, I), in 30–84% yields. The halogenation products of 1-nitro-2-piperidinopropene (**1e**) decomposed during the separation. These compounds are all new and were identified by spectral data. The NMR spectra for **2a–j** (X = Cl, Br, I) showed the same pattern as that of the corresponding **1a–j**, except that an absorption of a =CH proton in the vicinity of 6.5 ppm was missing. The IR spectra showed also a weak absorption near 3150 cm^{-1} except for the tertiary β-halo-β-nitroenamines **2j**. These results have shown that **2a–i** have the same intramolecular NH···O=N hydrogen-bonded chelate structure as the corresponding **1a–i**.[12]

The reaction of **1a–j** with *o*-nitrobenzenesulfenyl chloride in dioxane under a nitrogen atmosphere gave the corresponding β-nitro-β-[(*o*-nitrophenyl)thio]enamines, **3a–j**, in 68–99% yields. These compounds also are all new and gave satisfactory elemental analyses. The NMR spectra showed the same pattern as that for the corresponding **2a–j** except with absorption for aromatic protons of four H at 8.7–7.0 ppm. The compounds **3a–i** also were found to exist in a chelated structure similar to that of the corresponding **2a–i**.

In the reaction of **1a–j** with thiocyanogen at 0 °C for 1.5 h, **1a** and **1b** produced only the corresponding β-thiocyanated products, **4a** and **4b**, in 50% and 81% yields, respectively. **1f** gave a mixture of **4f** and the 2-aminothiazole derivative, **5f**, which is a cyclization product of **4f**, and **1h** also gave a mixture of **4h** and **6h**. The substrates **1c**, **1d**, **1g**, and **1i** yielded only the corresponding cyclization products **6c**, **6d**, **6g**, and **6i** under the same conditions, respectively. Compounds **4a**, **4b**, **4f**, and **4h** were purified by recrystallization from solvents without isomerization. However, these compounds were quantitatively isomerized into the corresponding cyclization products, **5a**, **6b**, **5f**, and **6h**, by stirring at room temperature with dichloromethane solution containing 0.1% acetic acid as a catalyst. The compounds **5** and/or **6** obtained from the reaction system are considered to be produced by $E \rightarrow Z$ isomerization of the preformed β-thiocyanato-β-nitroenamines, **4**, followed by cyclization catalyzed by the byproduct thiocyanic acid. The results of the reaction of 1 with thiocyanogen are summarized in Table I. The compounds **4a**, **4b**, **4h**, **4j**, and **6b–i** are all new and gave satisfactory elemental analyses. The IR spectra for **4** showed a ν(CN) at 2150–2160 cm^{-1} and a weak absorption at 3140–3190 cm^{-1}, except for **4j**, which was assigned to the intramolecular hydrogen-bonded ν(NH). The NMR spectra for **4** showed the same pattern as that for the corresponding **2**, respectively. The structure of **5** was confirmed by the elemental analyses, spectral data, and comparison of melting points with those of authentic samples. The IR spectra for **6** showed a weak ν(NH) absorption at 3320–3360 cm^{-1} and strong absorptions at 1565–1599 and 1319–1326 cm^{-1}, which were assigned to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively. The NMR spectra for **6b**, **6c**, **6g**, and **6h** showed a broad =NH absorption at δ 7.1–6.7 and a sharp NCH_3 or NCH_2 singlet at δ 3.39–3.08 or 5.14–4.85.

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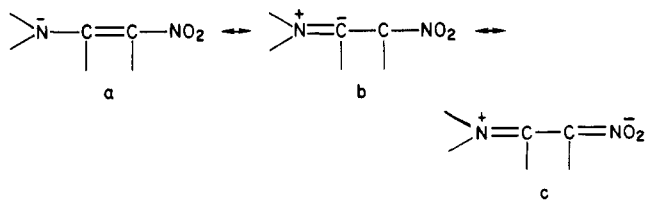
Scheme IV



It has been found that the primary and secondary β-nitroamines reacted with electrophiles at the β-position exclusively to give the β-substituted β-nitroenamines or their isomerized products. Consequently, the electrophilic reactivity of the β-nitroenamines can be accounted for by the contribution of a resonance structure **b** (Scheme IV) analogously to β-aminoenones.[15,16]

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Nihonbunko IRG spectrophotometer. NMR spectra were recorded on a Hitachi R24B (60 MHz) instrument and, except where noted, in $CDCl_3$, and chemical shifts are expressed in δ relative to Me_4Si as the internal standard. Splitting pattern abbreviations are as follows: s, singlet; d, doublet; m, multiplet. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University.

Analysis. Satisfactory analyses (±0.3%) for C, H, N, and halogen or S were reported for **2a–4**, **3a–j**, **4a–j**, and **6b–i**. The preparation of N-substituted β-nitroenamines, **1a–e**, was described in the previous paper;[12] **1f–j** were prepared by the reaction of α-nitroacetophenone with ammonia and/or amines similarly to that of **1a–e**, respectively. **1f**: yield 84%; mp 105–106 °C[17] (CCl_4). **1g**: yield 70%; mp 70–71 °C (CCl_4); IR ($CHCl_3$) 3180 cm^{-1} [ν(NH)]; NMR ($CDCl_3$) 10.1 (br, 1 H), 7.5 (m, 5 H), 7.67 (s, 1 H), 2.98 (d, J = 6 Hz, 3 H). **1h**: yield 60%; mp 90–91 °C[17] CCl_4). **1i**: yield 63%; mp 125–126 °C[17] (EtOH). **1j**: yield 48%; mp 114–115 °C[17] (CCl_4).

General Procedure for Preparation of β-Halo-β-nitroenamines 2a–j (X = Cl, Br, I) by Reaction of 1a–j with NXS. To a solution of 1 (10 mmol) in benzene/carbon tetrachloride (1/1, v/v) or benzene/chloroform (1/2, v/v) (20 time mass of 1) was added NXS (10.5 mmol) under a nitrogen atmosphere in the dark at 5 °C, and then the mixture was stirred for 1–2 h at room temperature. The resulting succinimide was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residual solid was recrystallized from the cited solvent to give the products **2a–j** (X = Cl, Br, I).

2-Amino-1-chloro-1-nitropropene (2a-Cl): mp 156–157 °C (EtOH); yield 30%; IR($CHCl_3$) 3480, 3290, 3170 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 9.7 (br, 1 H), 9.35 (br, 1 H), 2.3 (s, 3 H).

1-Chloro-2-(methylamino)-1-nitropropene (2b-Cl): mp 130–131 °C (benzene/CCl_4); yield 53%; IR ($CHCl_3$) 3120 cm^{-1} [ν(NH)]; NMR 11.05 (br, 1 H), 3.22 (d, J = 6 Hz, 3 H), 2.33 (s, 3 H).

2-(Benzylamino)-1-chloro-1-nitropropene (2c-Cl): mp 76–77 °C (CCl_4); yield 57%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.35 (br, 1 H), 7.35 (s, 5 H), 4.65 (d, J = 6 Hz, 2 H), 2.35 (s, 3 H).

1-Amino-2-chloro-2-nitro-1-phenylethylene (2f-Cl): mp 140–141 °C (EtOH); yield 86%; IR ($CHCl_3$) 3470, 3290, 3170 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 9.7 (br, 1 H), 9.3 (br, 1 H), 7.48 (s, 5 H).

2-Chloro-1-(methylamino)-2-nitro-1-phenylethylene (2g-Cl): mp 110–111 °C (CCl_4); yield 90%; IR ($CHCl_3$) 3150 cm^{-1} [ν(NH)]; NMR 10.8 (br, 1 H), 7.5 (m, 5 H), 2.90 (d, J = 6 Hz, 3 H).

1-(Benzylamino)-2-chloro-2-nitro-1-phenylethylene (2h-Cl): mp 144–145 °C (CCl_4); yield 69% IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 10.95 (br, 1 H), 7.3 (m, 10 H), 4.28 (d, J = 6 Hz, 2 H).

1-Anilino-2-chloro-2-nitro-1-phenylethylene (2i-Cl): mp 130 °C (CCl_4); yield 66%; IR ($CHCl_3$) 3150 cm^{-1} [ν(NH)]; NMR 12.2 (br, 1 H), 7.3 (m, 10 H).

2-Chloro-2-nitro-1-phenyl-1-piperidinoethylene (2j-Cl): mp 159–160 °C (benzene/CCl_4); yield 77%; NMR 7.54 (s, 5 H), 3.29 (m, 4 H), 1.78 (m, 6 H).

2-Amino-1-bromo-1-nitropropene (2a-Br): mp 131 °C (EtOH); yield 44%; IR ($CHCl_3$) 3470, 3280, 3170 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 9.85 (br, 1 H), 9.4 (br, 1 H), 2.26 (s, 3 H).

1-Bromo-2-(methylamino)-1-nitropropene (2b-Br): mp 97 °C (EtOH); yield 44%; IR ($CHCl_3$) 3130 cm^{-1} [ν(NH)]; NMR 11.2 (br, 1 H), 3.18 (d, J = 6 Hz, 3 H), 2.42 (s, 3 H).

2-(Benzylamino)-1-bromo-1-nitropropene (2c-Br): mp 89 °C (EtOH); yield 57%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 11.34 (br, 1 H), 7.3 (s, 5 H), 6.63 (d, J = 6 Hz, 2 H), 2.4 (s, 3 H).

2-Anilino-1-bromo-1-nitropropene (2d-Br): mp 91 °C (EtOH); yield 26%; IR ($CHCl_3$) 3150 cm^{-1} [ν(NH)]; NMR 12.5 (br, 1 H), 7.3 (m, 5 H), 2.38 (s, 3 H).

1-Amino-2-bromo-2-nitro-1-phenylethylene (2f-Br): mp 165–166 °C (benzene/CCl_4); yield 59%; IR ($CHCl_3$) 3460, 3280, 3180 cm^{-1} [ν(NH)]; NMR 9.8 (br, 1 H), 9.4 (br, 1 H), 7.43 (s, 5 H).

2-Bromo-1-(methylamino)-2-nitro-1-phenylethylene (2g-Br): mp 135–136 °C (EtOH); yield 75%; IR ($CHCl_3$) 3150 cm^{-1} [ν(NH)]; NMR 11.0 (br, 1 H), 7.5 (m, 5 H), 2.9 (d, J = 6 Hz, 3 H).

1-(Benzylamino)-2-bromo-2-nitro-1-phenylethylene (2h-Br): mp 137–138 °C (CCl_4); yield 54%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 11.2 (br, 1 H), 7.4 (m, 10 H), 4.35 (d, J = 6 Hz, 2 H).

1-Anilino-2-bromo-2-nitro-1-phenylethylene (2i-Br): mp 139–140 °C (EtOH); yield 81%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 12.3 (br, 1 H), 7.2 (m, 10 H).

2-Bromo-2-nitro-1-phenyl-1-piperidinoethylene (2j-Br): mp 149–150 °C (benzene/CCl_4); yield 53%; NMR 7.52 (s, 5 H), 3.28 (m, 4 H), 1.78 (m, 6 H).

2-Amino-1-iodo-1-nitropropene (2a-I): mp 136–137 °C (EtOH); yield 40%; IR ($CHCl_3$) 3480, 3290, 3160 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 10.7 (br, 1 H), 9.25 (br, 1 H), 2.35 (s, 3 H).

1-Iodo-2-(methylamino)-1-nitropropene (2b-I): mp 117 °C (EtOH); yield 87%; IR ($CHCl_3$) 3120 cm^{-1} [ν(NH)]; NMR 11.6 (br, 1 H), 3.2 (d, J = 6 Hz, 3 H), 2.5 (s, 3 H).

2-(Benzylamino)-1-iodo-1-nitropropene (2c-I): mp 107–108 °C (EtOH); yield 52%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.85 (br, 1 H); 7.2 (s, 5 H), 4.86 (d, J = 6 Hz, 2 H), 2.5 (s, 3 H).

2-Anilino-1-iodo-1-nitropropene (2d-I): mp 118 °C (EtOH); yield 53%; IR ($CHCl_3$) 3150 cm^{-1} [ν(NH)]; NMR 12.83 (br, 1 H); 7.3 (m, 5 H), 2.45 (s, 3 H).

1-Amino-2-iodo-2-nitro-1-phenylethylene (2f-I): mp 140–141 °C (EtOH); yield 48%; IR ($CHCl_3$) 3470, 3270, 3180 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 10.1 (br, 1 H), 9.4 (br, 1 H), 7.37 (s, 5 H).

2-Iodo-1-(methylamino)-2-nitro-1-phenylethylene (2g-I): mp, 173–174 °C (EtOH); yield 76%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.25 (br, 1 H), 7.5 (m, 5 H), 2.98 (d, J = 6 Hz, 3 H).

1-(Benzylamino)-2-iodo-2-nitro-1-phenylethylene (2h-I): mp 150–151 °C (EtOH); yield 63%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 11.42 (br, 1 H), 7.3 (m, 10 H), 4.33 (d, J = 6 Hz, 2 H).

1-Anilino-2-iodo-2-nitro-1-phenylethylene (2i-I): mp 172–173 °C (EtOH); yield 66%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 12.35 (br, 1 H), 7.2 (m, 10 H).

2-Iodo-2-nitro-1-phenyl-1-piperidinoethylene (2j-I): mp 136 °C (EtOH); yield 84%; NMR 7.51 (s, 5 H), 3.2 (m, 4 H), 1.78 (m, 6 H).

General Procedure for the Preparation of β-Nitro-β-[(o-nitrophenyl)thio]enamines 3a–j by the Reaction of 1a–j with o-Nitrobenzenesulfenyl Chloride. To a solution of 1 (10 mmol) and pyridine (11 mmol) in dioxane (20 times mass of 1) was slowly added powdered o-nitrobenzenesulfenyl chloride (10 mmol) under a nitrogen atmosphere at room temperature, and then the mixture was refluxed with stirring for 20–30 min. The reaction mixture was poured into water, and the resulting preciptate was collected by filtration. The residues were purified by column chromatography on silica gel (CH_2Cl_2) to give the products **3a-j**.

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2-Amino-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3a): mp 189–190 °C; yield 94%; IR ($CHCl_3$) 3470, 3280, 3170 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 10.1 (br, 1 H). 9.7 (br, 1 H), 8.4–7.1 (m, 4 H), 2.35 (s, 3 H).

2-(Methylamino)-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3b): mp 186–187 °C; yield 99%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.4 (br, 1 H), 8.4–7.0 (m, 4 H). 3.25 (d, J = 6 Hz, 3 H), 2.48 (s, 3 H).

2-(Benzylamino)-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3c): mp 156–157 °C; yield 93%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.3 (br, 1 H), 8.3–7.0 (m, 9 H), 4.73 (d, J = 6 Hz, 2 H), 2.48 (s, 3 H).

2-Anilino-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3d): mp 164–165 °C; yield 91%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 12.57 (br, 1 H), 8.4–7.0 (m, 9 H), 3.4 (s, 3 H).

1-Nitro-1-[(*o*-nitrophenyl)thio]-2-piperidinopropene (3e): mp 168–169 °C; yield 68%; NMR 8.4–7.1 (m, 4 H), 3.46 (m, 4 H), 2.65 (s, 3 H), 1.85 (m, 6 H).

1-Amino-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3f): mp 219–220 °C; yield 90%; IR ($CHCl_3$) 3460, 3300, 3150 cm^{-1} [ν(NH)]; NMR 10.2 (br, 1 H), 9.8 (br, 1 H), 8.4–7.1 (m, 9 H).

1-(Methylamino)-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3g): mp 163–164 °C; yield 91%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.03 (br, 1 H), 8.1–7.0 (m, 9 H), 2.85 (d, J = 6 Hz, 3 H).

1-(Benzylamino)-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylpropene (3h): mp 188–190 °C; yield 92%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.13 (br, 1 H), 8.2–7.0 (m, 14 H), 4.38 (d, J = 6 Hz, 2 H).

1-Anilino-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3i): mp 197 °C; yield 69%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 12.5 (br, 1 H), 8.3–7.0 (m, 14 H).

2-Nitro-2-[(*o*-nitrophenyl)thio]-1-phenyl-1-piperidinoethylene (3j): mp 136–137 °C; yield 83%; NMR 8.3–7.2 (m, 9 H), 3.3 (m, 4 H), 1.85 (m, 6 H).

Reaction of 1a–j with Thiocyanogen. To a solution of 1 (10 mmol) in dichloromethane (20 times mass of 1) was added with stirring at −15 °C a dichloromethane solution of thiocyanogen (10 mmol) which had previously prepared from lead thiocyanate and bromine at −15 °C, and then the mixture was stirred for 1.5 h at 0 °C or for 2–4 h at room temperature. The reaction mixture was washed with cold water and then dried with sodium sulfate. The solvent was evaporated in vacuo, and fractional precipitation of the residue from solvents afforded 4 and 5 or 6. The results of the reaction are shown in Table I.

2-Amino-1-nitro-1-thiocyanatopropene (4a): IR ($CHCl_3$) 3470, 3300, 3160 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR (Me_2SO-d_6) 9.9 (br, 1 H), 9.3 (br, 1 H), 2.4 (s, 3 H).

2-(Methylamino)-1-nitro-1-thiocyanatopropene (4b): IR ($CHCl_3$) 3140 [ν(NH)], 2150 cm^{-1} [ν(CN)]; NMR 10.9 (br, 1 H), 3.27 (d, J = 6 Hz, 3 H), 2.58 (s, 3 H).

1-Amino-2-nitro-1-phenyl-2-thiocyanatoethylene (4f): IR ($CHCl_3$) 3460, 3300, 3160 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR (Me_2SO-d_6) 10.1 (br, 1 H), 9.8 (br, 1 H), 7.5 (s, 5 H).

1-(Benzylamino)-2-nitro-1-phenyl-2-thiocyanatoethylene (4h): IR ($CHCl_3$) 3190 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR 11.0 (br, 1 H), 7.6 (m, 10 H), 4.35 (d, J = 6 Hz, 2 H).

2-Nitro-1-phenyl-1-piperidino-2-thiocyanatoethylene (4j): IR ($CHCl_3$) 2150 cm^{-1} [ν(CN)]; NMR 7.6 (m, 5 H), 3.24 (m, 4 H), 1.85 (m, 6 H).

2-Imino-3,4-dimethyl-5-nitro-4-thiazoline (6b): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 5.8 (br, 1 H), 3.39 (s, 3 H), 2.71 (s, 3 H).

3-Benzyl-2-imino-4-methyl-5-nitro-4-thiazoline (6c): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.3 (s, 5 H), 7.1 (br, 1 H), 5.14 (s, 2 H), 2.6 (s, 3 H).

2-Imino-4-methyl-5-nitro-3-phenyl-4-thiazoline (6d): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.5 (m, 5 H), 7.1 (br, 1 H), 2.38 (s, 3 H). [ν(NH)]; NMR 7.5 (m 5 H), 7.1 (br, 1 H), 2.38 (s, 3H).

2-Imino-3-methyl-5-nitro-4-phenyl-4-thiazoline (6g): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.4 (m, 5 H), 7.05 (br, 1 H), 3.08 (s, 3 H).

3-Benzyl-2-imino-5-nitro-4-phenyl-4-thiazoline (6h): IR ($CHCl_3$) 3320 cm^{-1} [ν(NH)]; NMR 7.5 (m, 10 H), 6.9 (br, 1 H), 4.85 (s, 2 H).

2-Imino-5-nitro-3,4-diphenyl-4-thiazoline (6i): IR ($CHCl_3$) 3360 cm^{-1} [ν(NH)]; NMR 7.5 (m, 10 H), 6.7 (br, 1 H).

General Procedure for the Preparation of 5 or 6 by Cyclization of 4. The solution of 4 in dichloromethane (20 times mass of 4) containing 0.1% acetoc acid was stirred for 2 h at room temperature. After removal of the solvent, the residue was recrystallized to give 5 or 6 in quantitative yields.

Registry No. **1a**, 95512-60-0; **1b**, 95512-61-1; **1c**, 95382-91-5; **1d**, 95382-89-1; **1e**, 95512-62-2; **1f**, 73025-50-0; **1g**, 73025-51-1; **1h**, 95512-63-3; **1i**, 73025-54-4; **1j**, 95512-64-4; **2a** (X = Cl), 95512-65-5; **2a** (X = Br), 95512-66-6; **2a** (X = I), 95512-67-7; **2b** (X = Cl), 95512-68-8; **2b** (X = Br), 95512-69-9; **2b** (X = I), 95512-70-2; **2c** (X = Cl), 95512-71-3; **2c** (X = Br), 95512-72-4; **2c** (X = I), 95512-73-5; **2d** (X = Br), 95512-74-6; **2d** (X = I), 95512-75-7; **2f** (X = Cl), 95512-76-8; **2f** (X = Br), 95512-77-9; **2f** (X = I), 95512-78-0; **2g** (X = Cl), 95512-79-1; **2g** (X = Br), 95512-80-4; **2g** (X = I), 95512-81-5; **2h** (X = Cl), 95512-82-6; **2h** (X = Br), 95512-83-7; **2h** (X = I), 95512-84-8; **2i** (X = Cl), 95512-85-9; **2i** (X = Br), 95512-86-0; **2i** (X = I), 95512-87-1; **2j** (X = Cl), 95512-88-2; **2j** (X = Br), 95512-89-3; **2j** (X = I), 95512-90-6; **3a**, 95512-91-7; **3b**, 95512-92-8; **3c**, 95512-93-9; **3d**, 95512-94-0; **3f**, 95512-96-2; **3g**, 95512-97-3; **3h**, 95512-98-4; **3i**, 95512-99-5; **3j**, 95513-00-1; **4a**, 95513-01-2; **4b**, 95513-02-3; **4f**, 95513-03-4; **4h**, 95513-04-5; **4j**, 95513-05-6; **5a**, 56682-07-6; **5f**, 95513-06-7; **6b**, 95513-07-8; **6c**, 95513-08-9; **6d**, 95513-09-0; **6g**, 95513-10-3; **6h**, 95513-11-4; **6i**, 95513-12-5; thiocyanogen, 505-14-6; nitromethyl phenyl ketone, 614-21-1; ammonia, 7664-41-7; methylamine, 74-89-5; benzylamine, 100-46-9; aniline, 62-53-3; piperidine, 110-89-4; 2-nitrobenzenesulfonyl chloride, 7669-54-7; acetic acid, 64-19-7.

Acenaphthenedithione

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As compared to α-diketones, little is known concerning the chemistry of α-dithiones. Early attempts to synthesize dithiobenzil (1) led to inconclusive results.[1] Later, a study