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Syntheses of 6-Substituted 7,8,9,10-Tetrahydrophenanthridin-7-ones through Sulfur Extrusion[1)]

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6-Substituted 7,8,9,10-tetrahydrophenanthridin-7-ones were synthesized by dehydrative cyclization and concomitant sulfur extrusion of 3-(2-acylaminophenylthio)-2-cyclohexen-1-ones with polyphosphoric acid.

Keywords——6-substituted 7,8,9,10-tetrahydrophenanthridin-7-one; dimedone; dehydrative cyclization; sulfur extrusion; analgesic activity

In the course of our synthetic studies on biologically active compounds using dimedone, tetronic acids, and tetramic acids,[2)] we planned to synthesize 6-substituted 7,8,9,10-tetrahydrophenanthridin-7-ones (**5**), because 6-amino-7,8,9,10-tetrahydrophenanthridines were reported to possess analeptic activity.[3)]

Denton *et al.*[4)] reported the synthesis of 6-substituted 7,8,9,10-tetrahydrophenanthridines by dehydrative cyclization of 2-acylaminocyclohexanes with polyphosphoric acid (PPA), with concomitant dehydrogenation, but the yield of the cyclodehydration reaction was relatively low, and multiple steps were required for the preparation of the intermediate 2-acylaminocyclohexanes. For application of the above method to the synthesis of **5**, 3-(2-acylaminophenyl)-5,5-dimethylcyclohexanones or the corresponding 2-cyclohexen-1-ones were considered as possible intermediates. In an attempt to prepare a 3-(2-acylaminophenyl)-5,5-dimethyl-2-cyclohexen-1-one, 3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one was treated with 2-chlorophenylmagnesium bromide, but 3-(2-chlorophenyl)-5,5-dimethyl-2-cyclohexen-1-one was not obtained, possibly because of steric hindrance. As a next approach, carbon–carbon bond formation reaction accompanied by sulfur extrusion[5)] was investigated. For example, when 2-phenyl-1,5-benzothiazepin-4-thione was treated with base, sulfur was extruded to give 4-phenylquinolin-2-thione.[5c)] Further, Oda *et al.*[5d)] reported that 1,5-dimethyl-3-phenyl-1*H*-pyrazolo[3,4-*d*]pyridazin-4(5*H*)-one was obtained by heating 4,7-dimethyl-2-phenyl-4*H*-pyridazino[4,5-*e*][1,3,4]thiadiazin-8(7*H*)-one.

Thus, 11-substituted 3,3-dimethyl-1,2,3,4-tetrahydrodibenzo[*b*,*f*][1,4]thiazepin-1-ones (**3**) were chosen as key intermediates for the preparation of **5**, because **5** could be obtained by base treatment or heating of **3**. There was another reason for choosing **3** as the key intermediates, *i.e.*, our interest in the biological activity of **3** as compared with that of the diaza analogs, 11-substituted 3,3-dimethyl-2,3,4,5-tetrahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-ones (**6**), the synthesis and analgesic activity of which were reported in our previous paper.[6)]

The known unstable 3-(2-aminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (**1**) ($R^1 = CH_3$)[7)] was treated with benzoyl chloride in pyridine to give 3-(2-benzoylaminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (**2a**) in 70% yield. When **2a** was allowed to react with excess PPA at 120—130 °C for 1.5 h, the cyclodehydration-sulfur extrusion product, 9,9-dimethyl-6-phenyl-7,8,9,10-tetrahydrophenanthridin-7-one (**5a**), was obtained in 85% yield. This result indicates that the cyclized product **3** is unstable to heating and readily extrudes sulfur to form the product **5** through the possible intermediate **4** even under cyclodehydration conditions.

For the purpose of examining the generality of this reaction, various electron-withdrawing and electron-releasing substituents were put on the phenyl ring of **2a**, and further, the phenyl ring was replaced by a heteroaromatic ring or an alkyl group, and these compounds were subjected to the reaction. The reactions occurred smoothly under the same reaction conditions as above in all cases, and the yields were moderate to fair. In the cases of **5b**, **5c**, **5f**, and **5g**, better yields were obtained by basic work-up, possibly because the initial product obtained by the general procedures mentioned above was the phosphoric acid salt.[6]

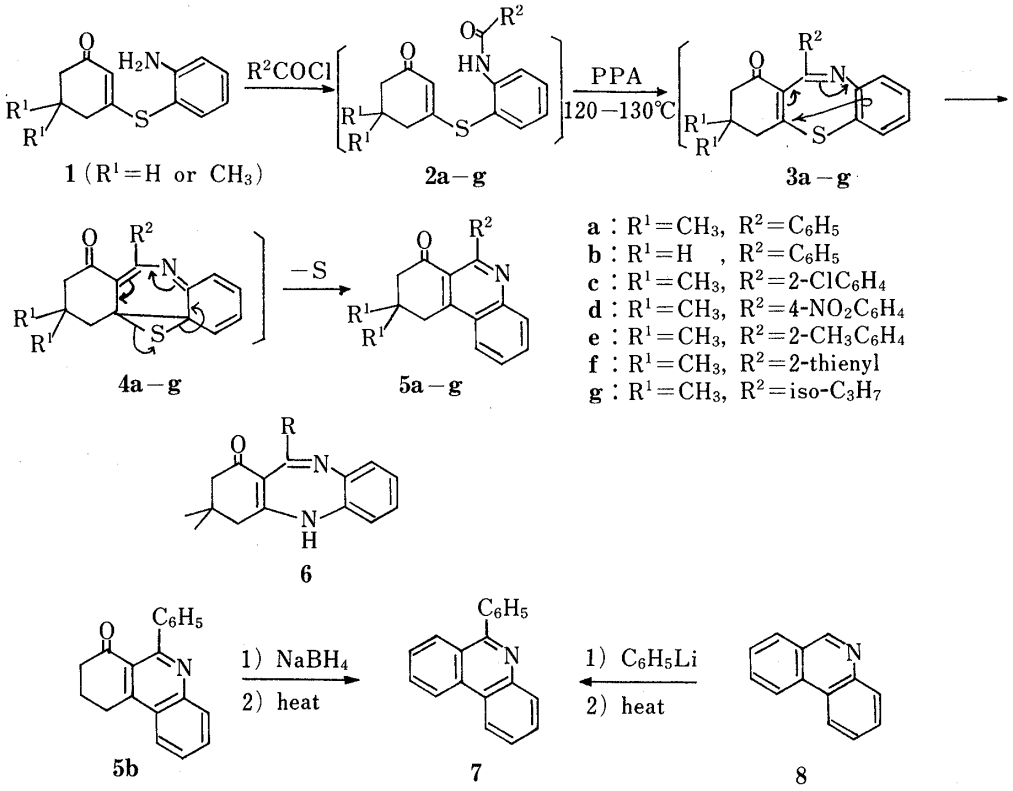

Chart 1

TABLE I. Melting Points, Yields, and Elemental Analyses of **5**

5	R^1	R^2	mp (°C) (Recryst. solvent)	Yield (%)	Formula	Analysis (%) Calcd (Found)		
						C	H	N
a	CH_3	C_6H_5	178—179 (MeOH)	85	$C_{21}H_{19}NO$	83.69 (83.94	6.35 6.23	4.65 4.66)
b	H	C_6H_5	147—148 (MeOH)	45	$C_{19}H_{15}NO$	83.49 (83.51	5.53 5.34	5.12 5.17)
c	CH_3	2-ClC_6H_4	144—147 (iso-PrOH–hexane)	91	$C_{21}H_{18}ClNO$	75.11 (75.05	5.40 5.31	4.17 4.16)
d	CH_3	4-$NO_2C_6H_4$	223.5—225 (benzene–hexane)	67	$C_{21}H_{18}N_2O_3$	72.82 (72.99	5.24 5.35	8.09 7.80)
e	CH_3	2-$CH_3C_6H_4$	129—130 (benzene–hexane)	87	$C_{22}H_{21}NO$	83.78 (83.92	6.71 6.66	4.44 4.35)
f	CH_3	2-Thienyl	155—156.5 (MeOH)	47	$C_{19}H_{17}NOS$	74.24 (74.33	5.57 5.48	4.56 4.51)
g	CH_3	iso-C_3H_7	115—117 (iso-PrOH–hexane)	32	$C_{18}H_{21}NO$	80.86 (80.88	7.92 7.97	5.24 5.25)

When **2f** was treated with PPA, 2-(2,2-dimethyl-4-oxopentyl)benzothiazole (**9**) was obtained in 30% yield as a by-product along with **5f** (47%). Although polyphosphate ester, stannic chloride, or formic acid was tested as the cyclodehydration reagent, no reaction occurred. Yields, melting points, microanalyses, infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectral data are listed in Tables I and II.

In order to confirm the structure **5**, **5b** was converted into the known 6-phenylphenanthridine (**7**) by sodium borohydride reduction and subsequent heating of the product in nitrobenzene. Its IR and ^{1}H-NMR spectra and melting point were identical with those of an authentic sample, prepared from phenanthridine (**8**) by addition of phenyllithium and subsequent dehydrogenation.[8)]

Next, we examined the cyclodehydrative-sulfur extrusion reaction with PPA of the dihydrogenated product of **2a**, 3-(2-benzoylaminophenylthio)-5,5-dimethylcyclohexanone (**11**), which was prepared by addition of 2-aminobenzenethiol to 5,5-dimethyl-2-cyclohexen-1-one (**10**)[7)] in the presence of Triton B, followed by benzoylation. However, no cyclodehydration-sulfur extrusion product was obtained in this case, and 2-phenylbenzothiazole (**12**) was isolated in 66% yield. This indicates that retro-Michael type reaction took place first and then the product cyclized to form **12**. Subsequently, base treatment of **2a** was carried out in order to examine the possibility of sulfur extrusion at this stage. When **2a** reacted with sodium hydride in dimethyl formamide (DMF), or sodium borohydride in pyridine, 2,3-dihydro-2,2-dimethyl-1*H*-phenothiazin-4(10*H*)-one (**13**)[8)] was obtained in 35 or 36% yield, respectively. These results mean that the sulfur extrusion reaction did not occur, but Smiles rearrangement, oxidation, hydrolysis, and then cyclization occurred consecutively in these cases. On the other hand, an alternative synthesis of **3a** was attempted. Treatment of 2-benzoyl-3-chloro-5,5-dimethyl-2-cyclohexen-1-one (**14**)[9)] with 2-aminobenzenethiol in

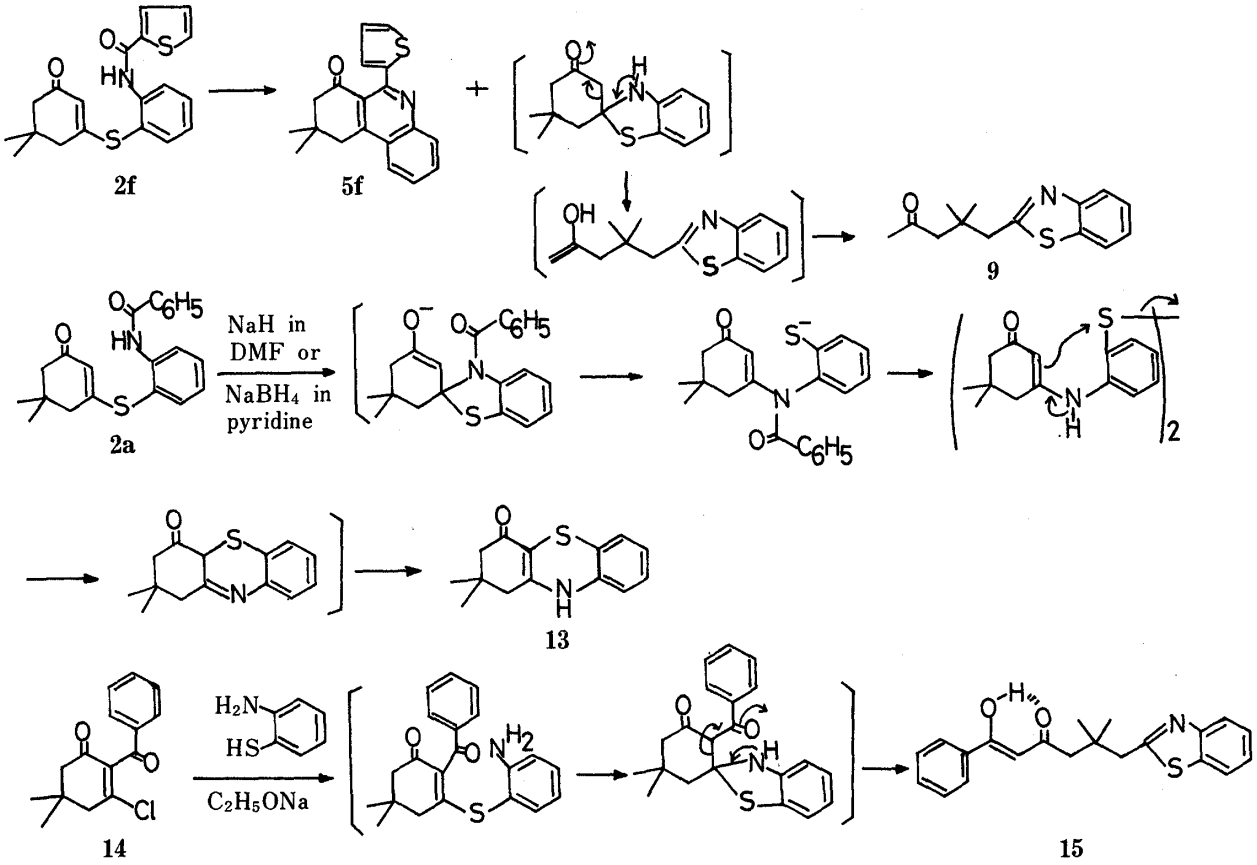

Chart 2

TABLE II. IR and ^{1}H-NMR Spectral Data for **5**

5	IR ν_{max}^{Nujol} cm^{-1}	^{1}H-NMR δ (J in Hz)[a]
a	1685, 1550, 1404, 1270, 1220, 760, 708	($CDCl_3$) 1.20 (6H, s, 2×CH_3), 2.64 and 3.35 (each 2H, s, 2×CH_2), 7.36—8.20 (9H, m, ArH)
b	1690, 1555, 1290, 1220, 1130, 950, 765, 710	($CDCl_3$) 2.33 (2H, quin, J=6.5, $CH_2C\underline{H}_2CH_2$), 2.74 (2H, t, J=6.5, $CC\underline{H}_2CH_2$), 3.42 (2H, t, J=6.5, $C\text{–}C\underline{H}_2CH_2$), 7.32—8.14 (9H, m, ArH)
c	1680, 1620, 1580, 1560, 1230, 1055, 945, 920, 760, 740	($CDCl_3$) 1.18 and 1.25 (each, 3H, s, 2×CH_3), 2.48 and 2.74 (each, 1H, d, J=15.5, CCH_2C), 3.30 and 3.40 (each 1H, d, J=18, CCH_2C), 7.36—8.24 (8H, m, ArH)
d	1685, 1550, 1510, 1340, 1220, 1110, 1090, 855, 845, 765	(DMSO-d_6) 1.14 (6H, s, 2×CH_3), 2.62 and 3.43 (each 2H, s, 2×CH_2), 7.60—8.30 (8H, m, ArH)
e	1680, 1550, 1215, 1085, 915, 765, 755, 735	($CDCl_3$) 1.18 (6H, s, 2×CH_3), 2.04 (3H, s, $ArCH_3$), 2.55 and 3.35 (3ach 2H, s, 2×CH_3), 7.10—8.20 (8H, m, ArH)
f	1695, 1550, 1275, 1230, 1080, 1050, 970, 855, 770, 735, 710	(DMSO-d_6) 1.12 (6H, s, 2×CH_3), 2.67 and 3.33 (each 2H, s, 2×CH_2), 6.96—8.16 (7H, m, ArH)
g	1685, 1615, 1565, 1270, 1230, 1165, 1095, 960, 870, 765	($CDCl_3$) 1.14 (6H, s, 2×CH_3), 1.32 (6H, d, J=6.5, $CH(C\underline{H}_3)_2$), 2.59 and 3.23 (each 2H, s, 2×CH_2), 4.14 (1H, sep, J=6.5, $C\underline{H}(CH_3)_2$), 7.43—8.02 (4H, m, ArH)

a) d, doublet; m, multiplet; quin, quintet; s, singlet; sep, septet.

ethanol in the presence of sodium ethoxide failed to give **3a** and resulted in the formation of 2-(2,2-dimethyl-4,6-dioxo-6-phenylhexyl)benzothiazole (**15**) in 43% yield.

In conclusion, the cyclodehydration-sulfur extrusion reaction of 3-(2-acylaminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (**2**) with PPA is quite general and provides a convenient method for the preparation of 6-substituted 7,8,9,10-tetrahydrophenanthridin-7-ones (**5**). Finally, when the compounds **5c** and **5f** were tested for analgesic activity by the phenylquinone writhing method, **5c** showed weak activity (25.4% in inhibition) at the dose of 50 mg/kg (using mice as the test animal), but **5f** was inactive. Pharmacological testing of the other compounds is now under way.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus, model MP-S3, and are uncorrected. IR and ^{1}H-NMR spectra were measured with a Hitachi 260-30 infrared spectrometer and a JEOL JNM-FX 200 (200 MHz) spectrometer, respectively, using tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were measured with a JEOL JMS-HX 100 spectrometer.

3-(2-Benzoylaminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (2a)——Benzoyl chloride (3.927 g, 27.94 mmol) was added dropwise to a solution of 3-(2-aminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (**1**) (R^1=CH_3) (6.273 g, 25.39 mmol) in dry pyridine (36 ml) with stirring and cooling, and the whole was stirred at room temperature overnight. Water was added to the mixture, and the precipitates formed were collected by filtration. The crude product was recrystallized from benzene–hexane to give 6.26 g (70%) of **2a** as colorless needles; mp 120—121 °C. IR ν_{max}^{Nujol} cm^{-1}: 3370, 1680, 1665, 1580, 1515, 1310, 1285, 1150, 1015, 850, 760, 720. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (6H, s, 2×CH_3), 2.21 (2H, s, CH_2), 2.40 (2H, s, CH_2), 5.53 (1H, s, =CHC), 7.12—8.74 (9H, m, ArH), 8.79 (1H, s, NH). *Anal.* Calcd for $C_{21}H_{21}NO_2S$: C, 71.77; H, 6.02; N, 3.99. Found: C, 71.74; H, 5.93; N, 4.01. Other amides (**2b—g**) were synthesized similarly, and used for the next reaction, after confirming that they gave a single spot on an SiO_2 thin layer chromatogram.

General Method for Synthesis of 6-Substituted 7,8,9,10-Tetrahydrophenanthridin-7-ones (5)——A mixture of a 3-(2-acylaminophenylthio)-2-cyclohexen-1-one (**2**) (4.56 mmol) and PPA (30 g) was stirred at 120—130 °C for 1.5 h. After the mixture had cooled to room temperature, water was added with stirring and ice-water cooling, and the whole was extracted three times with chloroform. The combined extract was washed with brine, dried over Na_2SO_4,

and concentrated to dryness under reduced pressure. The crude product was recrystallized from the appropriate solvent, or purified by SiO_2 column chromatography (chloroform) followed by recrystallization to give **5a**, **5d**, **5e**. In the cases of **5b**, **5c**, **5f**, and **5g**, when the reaction was over, dil. NaOH solution was added to the reaction mixture with stirring and ice-water cooling to give pH 8—9, and then the whole was extracted with chloroform. The following procedures were the same as above. Yields, melting points, microanalyses, IR and ^{1}H-NMR spectral data are listed in Tables I and II.

6-Phenylphenanthridine (7) from 8——According to the literature,[10] 2.44 g (86%) of **7** was obtained starting with 2 g of phenanthridine (**8**); mp 104—106 °C (lit.,[10] mp 104—105 °C).

6-Phenylphenanthridine (7) from 5b——A mixture of 6-phenyl-7,8,9,10-tetrahydrophenanthridin-7-one (**5b**) (0.745 g, 2.73 mmol) and sodium borohydride (0.103 g, 2.73 mmol) in ethanol (45 ml) was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, then water was added and the whole was extracted three times with chloroform. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give a powder, which was dissolved in nitrobenzene (2.5 ml) without further purification. The solution was heated at reflux temperature for 1.5 h. Nitrobenzene was evaporated off under reduced pressure and the residue was dissolved in ethanol (5 ml). A solution of picric acid (0.758 g, 3.31 mmol) in ethanol (11 ml) was added to the above solution and the whole was stirred for 30 min. Precipitates formed were collected by filtration, and then dissolved in a 5 N NaOH solution. The mixture was extracted three times with chloroform and the combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 0.608 g (87%) of **7** as a solid, which was recrystallized from benzene–petroleum ether; mp 105—105.5 °C. IR ν_{max}^{Nujol} cm^{-1}: 1615, 1585, 1565, 1335, 960, 770, 705. ^{1}H-NMR ($CDCl_3$) δ: 7.32—8.70 (13H, m, ArH). The IR and ^{1}H-NMR spectral data were identical with those of an authentic sample of **7**.

2-(2,2-Dimethyl-4-oxopentyl)benzothiazole (9)——After SiO_2 column chromatography (chloroform) of the crude products obtained by the general method for the synthesis of **5**, **9** (0.907 g, 30%) was isolated from the more polar fraction as an oil along with **5f** (1.894 g, 47%), which was obtained from the less polar fraction, starting with 4.65 g (13 mmol) of **2f**. **9**: bp 126 °C (1 Torr) (oven temperature in bulb-to-bulb distillation). IR ν_{max}^{neat} cm^{-1}: 1710, 1615, 1510, 1290, 1150, 1100, 1065, 1015, 760. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (6H, s, 2 × CH_3), 2.13 (3H, s, $COCH_3$), 2.50 (2H, s, CH_2), 3.19 (2H, s, CH_2), 7.25—7.97 (4H, m, ArH). Calcd exact mass for $C_{14}H_{17}NOS$: 247.1031. Found: 247.1033.

3-(2-Benzoylaminophenylthio)-5,5-dimethylcyclohexanone (11)——Triton B (2 drops) was added to a solution of 5,5-dimethyl-2-cyclohexen-1-one (**10**) (2 g, 16.13 mmol) and 2-aminobenzenethiol (2.02 g, 16.13 mmol) in dioxane (20 ml), and the whole was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, then water was added and the whole was extracted three times with ethyl acetate. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give an oil (4 g), which was dissolved in dry pyridine. Benzoyl chloride (2.48 g, 17.66 mmol) was added to the above solution with stirring and cooling, and the whole was allowed to stand at room temperature overnight. After addition of water, the mixture was extracted three times with chloroform. The combined extract was washed with water, dil. HCl solution and brine, dried over Na_2SO_4, and concentrated under reduced pressure to furnish a gum. The crude product was purified by SiO_2 column chromatography (benzene–ethyl acetate = 4 : 1), and recrystallization from benzene–hexane to give 3.689 g (65%) of **11** as colorless needles; mp 93—96 °C. IR ν_{max}^{Nujol} cm^{-1}: 3350, 1710, 1680, 1580, 1510, 1305, 1260, 1075, 1030, 895, 760. ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.67 (1H, t, J = 12 Hz, $SCHCH_2C$), 1.88 (1H, m, $SCHCH_2C$), 2.09 (2H, d, J = 8 Hz, $COCH_2C$), 2.24 (1H, t, J = 12 Hz, $COCH_2CHS$), 2.60 (1H, m, $COCH_2CHS$), 3.26 (1H, tt, J = 12, 4 Hz, $SCHCH_2$), 7.06—8.68 (9H, m, ArH), 9.45 (1H, br s, NHCO). Calcd exact mass for $C_{21}H_{23}NO_2S$: 353.1450. Found: 353.1403.

2-Phenylbenzothiazole (12)——A mixture of 3-(2-benzoylaminophenylthio)-5,5-dimethylcyclohexanone (**11**) (1 g, 2.83 mmol) and PPA (19 g) was stirred and heated at 120—130 °C for 1.5 h. The mixture was cooled and treated with a 10 N NaOH solution. The whole was extracted three times with chloroform, and the combined extract was washed with water and brine. After being dried over Na_2SO_4, the solution was concentrated under reduced pressure to give an oil, which was purified by SiO_2 column chromatography (benzene) and recrystallization from hexane to give 0.392 g, (66%) of **12** as colorless needles; mp 115—116 °C (lit.,[11] mp 114 °C). IR ν_{max}^{Nujol} cm^{-1}: 1505, 1475, 1310, 1220, 960, 765, 730.[11] ^{1}H-NMR ($CDCl_3$) δ: 7.34—7.62 (5H, m, ArH), 8.0—8.16 (4H, m, ArH). *Anal.* Calcd for $C_{13}H_9NS$: C, 73.89; H, 4.30; N, 6.63. Found: C, 73.87; H, 4.14; N, 6.65.

2,3-Dihydro-2,2-dimethyl-1*H*-phenothiazin-4(10*H*)-one (13)——a) By Sodium Hydride Treatment: 3-(2-Benzoylaminophenylthio)-5,5-dimethyl-2-cyclohexen-1-one (**2a**) (0.3 g, 0.85 mmol) was added to a suspension of sodium hydride (60% purity, 31 mg, 0.85 mmol) in dry DMF (5 ml), and the whole was stirred at room temperature overnight. Water was added under ice-water cooling and the mixture was extracted three times with chloroform. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give a powder, which was crystallized from chloroform–methanol to give 73 mg (35%) of **13** as orange plates; mp 261—266 °C (lit.,[8] mp 262—263 °C. IR ν_{max}^{Nujol} cm^{-1}: 3240, 1580, 1570, 1525, 1310, 1265, 1150, 1125, 750. ^{1}H-NMR (DMSO-d_6) δ: 0.98 (6H, s, 2 × CH_3), 2.12 (2H, s, CH_2), 2.18 (2H, s, CH_2), 6.48—6.88 (4H, m, ArH), 8.72 (1H, br s, NH). *Anal.* Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71. Found: C, 68.76; H, 5.91; N, 5.43.

b) By Sodium Borohydride Treatment: Sodium borohydride (0.239 g, 5.69 mmol) was added to a solution of **2a**

(1 g, 2.85 mmol) in pyridine (10 ml) and the whole was stirred at room temperature overnight. After addition of water, the mixture was extracted three times with chloroform. The combined extract was washed with dil. HCl solution, saturated $NaHCO_3$ solution, water, and brine successively, and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue, which was purified by SiO_2 column chromatography (chloroform–methanol = 100 : 1) followed by recrystallization from chloroform–methanol to furnish 0.25 g (36%) of **13**. Melting point, IR and ^{1}H-NMR spectral data were identical with those of the sample obtained by procedure (a).

2-(2,2-Dimethyl-4,6-dioxo-6-phenylhexyl)benzothiazole (15)——2-Aminobenzenethiol (0.543 g, 4.34 mmol) and 2-benzoyl-3-chloro-5,5-dimethyl-2-cyclohexen-1-one (**14**) (1.14 g, 4.34 mmol) were added to a solution of sodium ethoxide [prepared from sodium (0.1 g, 4.34 mg atom) and ethanol (15 ml)] with stirring at room temperature. The mixture was stirred for 1 h at the same temperature and then heated for 1 h at reflux temperature. After cooling, the mixture was concentrated under reduced pressure, the residue was diluted with water, and the whole was extracted three times with chloroform. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give an orange oil, which was purified by SiO_2 column chromatography (chloroform) to furnish 0.628 g (43%) of **15** as an orange oil; bp 222 °C (0.5 Torr) (oven temperature in bulb-to-bulb distillation). IR ν_{max}^{neat} cm^{-1}: 1600, 1275, 1185, 1090, 955, 760. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (6H, s, 2 × CH_3), 2.47 (2H, s, CH_2), 3.16 (2H, s, CH_2), 6.21 (1H, s, =CHCO), 7.15—7.95 (9H, m, ArH), 16.12 (1H, br s, =COH). Calcd exact mass for $C_{21}H_{21}NO_2S$: 351.1293. Found: 351.1256.

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References and Notes

1) Preliminary communication; K. Matsuo, M. Ohta, and K. Tanaka, *Chem. Lett.*, **1985**, 291.
2) K. Tanaka, K. Matsuo, Y. Nakaizumi, Y. Morioka, Y. Takashita, Y. Tachibana, Y. Sawamura, and S. Kohda, *Chem. Pharm. Bull.*, **27**, 1901 (1979); K. Matsuo, I. Kitaguchi, Y. Takata, and K. Tanaka, *ibid.*, **28**, 2494 (1980); K. Tanaka, K. Matsuo, A. Nakanishi, M. Jo, H. Shiota, M. Yamaguchi, S. Yoshino, and K. Kawaguchi, *ibid.*, **32**, 3291 (1984); K. Matsuo and K. Tanaka, *ibid.*, **32**, 3724 (1984); K. Matsuo, M. Kimura, N. Takai, and K. Tanaka, *ibid.*, **32**, 4197 (1984); K. Matsuo and K. Tanaka, *Yakugaku Zasshi*, **104**, 1004 (1984).
3) B. L. Hollingsworth and V. Petrow, *J. Chem. Soc.*, **1960**, 263.
4) D. A. Denton, R. K. Smalley, and H. Suschitzky, *J. Chem. Soc.*, **1964**, 2421.
5) *a*) D. H. R. Barton and B. J. Willis, *Chem. Commun.*, **1970**, 1225; *b*) P. Loeliger and E. Flückinger, *Organic Syntheses*, **55**, 127 (1976); *c*) D. H. R. Barton and W. D. Ollis "Comprehensive Organic Chemistry," Vol. 4, ed. by P. G. Sammes, Pergamon Press, Oxford, 1979, pp. 1161—1166; *d*) K. Kaji, H. Nagashima, S. Nagao, and H. Oda, *Chem. Pharm. Bull.*, **32**, 4437 (1984).
6) K. Matsuo, M. Yoshida, M. Ohta, and K. Tanaka, *Chem. Pharm. Bull.*, **33**, 4057 (1985).
7) G. A. Hiegel and P. Burk, *J. Org. Chem.*, **38**, 3637 (1973).
8) S. Miyano, N. Abe, K. Sumoto, and K. Teramoto, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 1146.
9) Y. Tamura, S. Fukumori, A. Wada, S. Okuyama, J. Adachi, and Y. Kita, *Chem. Pharm. Bull.*, **30**, 1692 (1982).
10) H. Gilman and R. D. Nelson, *J. Am. Chem. Soc.*, **70**, 3316 (1948).
11) "The Sadtler Standard Spectra—Standard Grating Spectra," Vol. 22, 21249K, Sadtler Research Laboratories, Inc., Philadelphia, 1971.