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Pyrimido-1,4-benzothiazines and -1,4-benzothiazepines. II.[1] Thermal and Photochemical Rearrangements of Pyrimido-1,4-benzothiazine Sulfonium Ylides

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Thermolysis of pyrimido-1,4-benzothiazine sulfonium ylides caused competitively [1,2] and [1,4]rearrangements, or β-elimination, depending upon the natures of the substituents in the ylide moiety. Ultraviolet irradiation of the methyl, ethyl and benzyl sulfonium ylides resulted exclusively in the [1,2]rearrangement followed by ring expansion leading to pyrimido-1,4-benzothiazepines. On the basis of some data, the reaction sequences of these rearrangements were discussed.

Keywords——carbonyl-stabilized cyclic sulfonium ylides; thermal [1,2] and [1,4] rearrangements; photochemical [1,2] rearrangements; β-elimination; ring-expansion

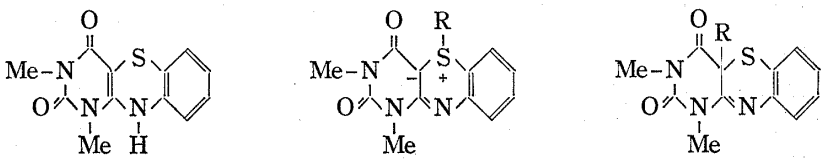
The thermal rearrangements of sulfonium ylides have been well investigated.[3] In particularly, allylsulfonium ylides have been shown to undergo thermally [2,3]sigmatropic rearrangement or Stevens-type ([1,2])rearrangement. Contrary to their abundance, the photo-induced rearrangements of sulfonium ylides are surprisingly rare because of their susceptibility to photocleavage of the dipolar sulfur-carbon bond to give products derived from carbene and ketene intermediates.[4,5] Only few examples of photo-induced [1,2]rearrangement of sulfonium ylides have been documented.[6]

Goldman[7,8] has reported some novel reactions in the pyrimido[5,4-*b*]-1,4-benzothiazine-dione system involving the formation of a stable ylide and its thermal [1,2]rearrangement. Previously, we demonstrated a convenient preparative method of 1,3-dimethyl-1,2,3,4-tetrahydro-10(*H*)-pyrimido[5,4-*b*]-1,4-benzothiazine-2,4-dione(I),[9,10] and had an occasion to examine the chemical natures of I[1] and the corresponding sulfonium ylides (IIa—d).

In this paper, we wish to describe our own results on the thermal and photochemical rearrangements of sulfonium ylides (II). The present observations are particularly interested in the following points; 1) The thermal rearrangement of the ylides (II) depends upon the nature of substituents in the ylide moiety. Occurrence of competing [1,2] and [1,4]rearrangements observed in the methyl and benzyl sulfonium ylides (IIa, d) is novel and has mechanistic implication. 2) Irradiation of the ylides causes exclusively [1,2]rearrangement followed by

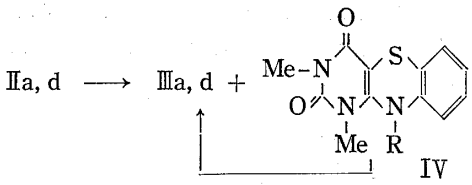
1) Part I: Y. Maki and T. Hiramitsu, *Chem. Pharm. Bull.* (Tokyo), **24**, 3135 (1976).
2) Location: *6-1, Higashi 5-chome, Mitahora, Gifu, 502, Japan.*
3) For a recent review, see B.M. Trost and L.S. Melvin, Jr., "Sulfur Ylides", Academic Press, New York, 1975, p. 108.
4) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).
5) B.M. Trost, *J. Am. Chem. Soc.*, **88**, 1587 (1966); *idem, ibid.*, **89**, 138 (1967).
6) For leading reference, see R.H. Fish, *Tetrahedron Letters*, **1969**, 1259.
7) J.M. Goldman and E.G. Andrews, as quoted in *Chem. Eng. News*, 1967 (July 10), 44. Abstract of papers, 1st International Congress of Heterocyclic Chemistry, New Mexico, 1967.
8) After completion of this work, we have learned that Goldman has referred to the photochemical rearrangement of the ylide without detail description in his patent (U.S. Patent 3483198).
9) Y. Maki, T. Hiramitsu, and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **22**, 1265 (1974).
10) This system has been prepared independently *via* alternative routes by Fenner (H. Fenner, *Arzneim. Forsch.*, **20**, 1815 (1970)) and by Goldman (references 7) and 8)).

ring expansion leading to 1,3-dimethyl-1,2,3,4,5,11-hexahydropyrimido-1,4-benzo[*b*]thiazepine-2,4-diones (V), although the latter step is significantly influenced by the nature of 4*a*-substituents of the [1,2]-rearranged products (III). This type of photoreaction provides a convenient preparative method of fused thiazepines.



I II III

a: R=CH_3, b: R=C_2H_5, C: R=iso-C_3H_7,
d: R=$C_6H_5CH_2$, e: R=CH_2=$CHCH_2$



in the case of
R=$C_6H_5CH_2$ a: R=CH_3, b: R=$C_6H_5CH_2$

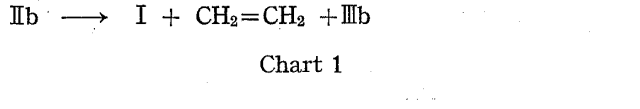


Chart 1

When I was treated with methyl, ethyl, and isopropyl iodides or benzyl bromide on ice cooling in dimethylformamide (DMF) in the presence of sodium hydride according to Goldman's procedure,[7,8] the corresponding ylides (IIa—d) were obtained in 50 to 80% yields, respectively. Analogous reaction of I with allyl iodide, however, resulted in the formation of 4*a*-allyl derivative (IIIe) (80%). Under employed conditions, allyl sulfonium ylide (IIe) was not obtained. No isolation of IIe can be ascribed to the occurrence of a facile [2,3]sigmatropic rearrangement of the initially formed IIe to IIIe.[3]

Upon heating of methyl sulfonium ylide (IIa) at 210—220°, 4*a*-methyl derivative (IIIa) (90%) and N-methyl derivative (IVa) (5%) were obtained. Benzyl sulfonium ylide (IId) was more unstable than IIa, and underwent smooth rearrangement in chloroform even at 34° to give 4*a*-benzyl derivative (IIId) (75%) and N-benzyl derivative (IVb) (25%) (by nuclear magnetic resonance (NMR).

Contrary to the case of N-methyl derivative (IVa), IVb rearranged to give 4*a*-benzyl derivative (IIIa) almost quantitatively upon heating it in DMSO at 150°.

In the cases of ethyl and isopropyl sulfonium ylides (IIb, c), which possess at least a β-hydrogen in the alkyl residue, β-elimination occurs preferentially rather than the rearrangements observed in the cases of IIa, d. Thermolysis of IIb in an NMR tube employing DMSO-d_6 as a solvent at rising temperature to 150° was monitored by taking NMR spectra. Thus, the formation of ethylene and a trace amount of 4*a*-ethyl derivative (IIIb) in addition to I was proved.

Physicochemical data of II,[11] III, and IV are consistent with their structures, *e.g.*, one of carbonyl stretching bands of IId appears at noticeable low frequency (1600 cm^{-1}), whereas these of IIId and IVb are observed at 1720 and 1640 cm^{-1} in their infrared (IR) spectra, respectively. The NMR spectra of IId, IIId, and IVb showed characteristic benzylmethylene protons

11) The ylide structure of this type of compound was confirmed by X-ray crystallographic study (*cf.* J.D. Schaefer and L.L. Read, *J. Am. Chem. Soc.*, **94**, 908 (1972).

at δ 3.73, 4.07 (AB-type quartet, J=12 Hz), δ 3.04, 3.30 (AB-type, quartet, J=12 Hz) and δ 4.66 (singlet), respectively (see Experimental part).

No interconversion between IIId and IVb was observed under the conditions similar to the rearrangement of IId to IIId and IVb, although employment of more drastic condition caused the conversion of IVb to IIId as mentioned above, presumably *via* homolytic cleavage of an N-benzyl linkage of IVb.[12] These facts accomodate to occurrence of competing [1,2] and [1,4]rearrangements.

In view of the conclusion[3,13] that have been drawn concerning the radical-pair mechanism of a number of anionic [1,2] (Stevens-type) rearrangement, often based on the observation of CIDNP, the rearrangement of ylides II to III appears to involve the radical-pair process.

Ollis, *et al.*[13] have shown that the anionic [1,4]rearrangement observed in 2-oxyanilinium ylides proceeds principally *via* the concerted sigmatropic process (see (A)) accompanied with the radical-pair process to some extent. Likewise, the present [1,4]rearrangement of IIa, d appeared to proceed primarily *via* a thermal orbital symmetry-allowed concerted process, although the inherent S_Ni character of this process could result in a relatively high activation energy.[13]

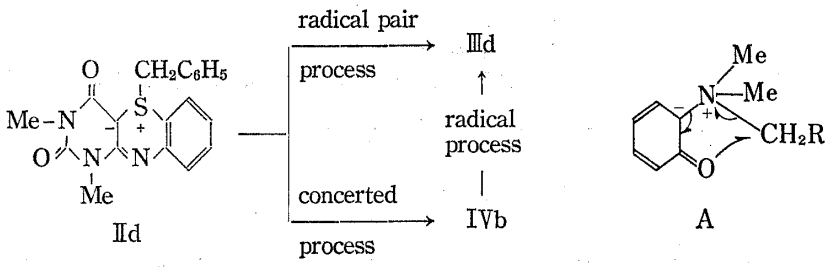


Chart 2

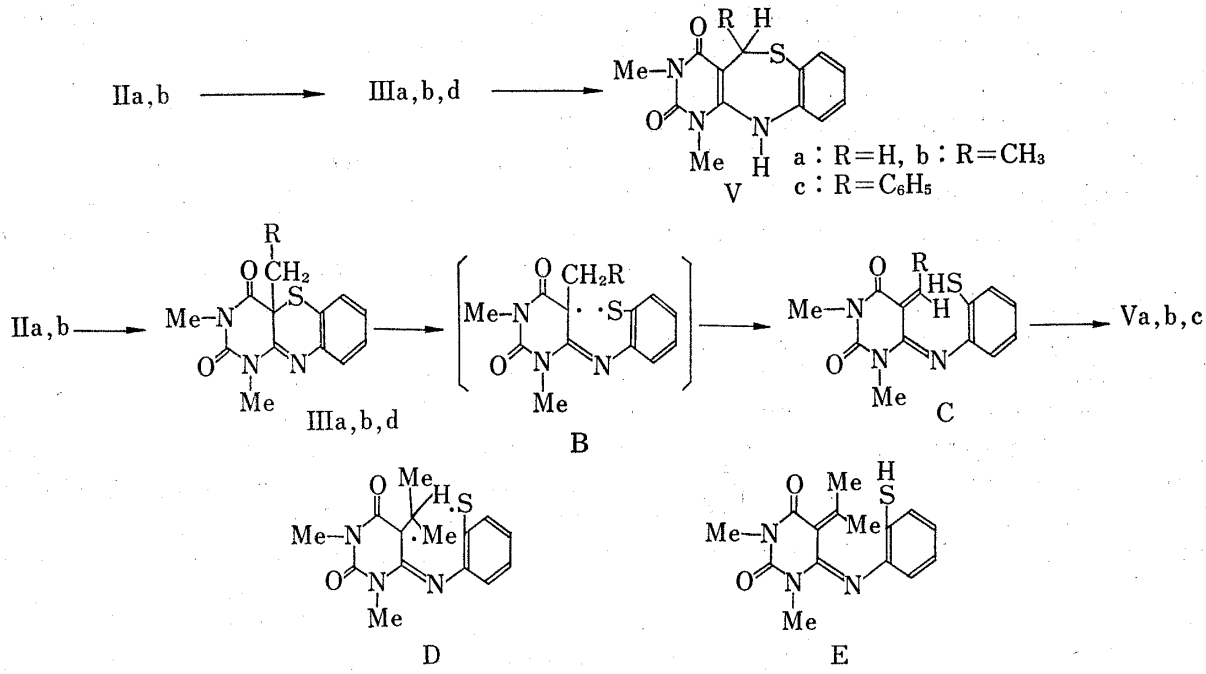


Chart 3

12) A similar N→C rearrangement has been observed in the N-benzyl-thiazolidene system (*cf.* J.E. Baldwin and J.A. Walker, *J. Am. Chem. Soc.*, **96**, 596 (1974)).

13) W.D. Ollis, I.O. Sutherland and Y. Thebtaranonth, *Chem. Commun.*, **1973**, 653, 654.

There have been some examples of the anionic [1,4]rearrangement of the ylide[13–17] in which an aromatic ring is involved as a function. These previous examples, however, are not accompanied with the [1,2]rearrangement. This can be ascribed to severe destruction of the aromaticity during the [1,2]rearrangement. In the present case, the primarily less aromaticity of the uracil ring in II appears to allow occurrence of the [1,2]rearrangement, together with the [1,4]rearrangement.

When IIa, b in methanol or ethanol were irradiated with 100W high pressure mercury arc lamp through a Pyrex filter under nitrogen for several hr, thiazepines (Va, b) were obtained in 80% and 90% yields, respectively. The short-period irradiation of IIb allowed to isolate IIIb in addition to Vb. 4*a*-Methyl, ethyl and benzyl derivatives (IIIa, b, d) also gave Va, b, c by analogous irradiation, whereas 4*a*-isopropyl derivative (IIIc) was recovered unchanged. Thus, IIIa, b must be an intermediate of the ring expansion of IIa, b to Va, b. The yields of the thiazepines (Va, b, c) depend largely upon degassing the sample.

It is notable that in sharp contrast to the thermal rearrangement, the photoconversion of IIa, b into Va, b involves a facile [1,2]rearrangement(photo-Stevens rearrangement) and [1,4]-rearrangement does not occur concurrently.

Unexpectedly, analogous irradiation of isopropyl sulfonium ylide (IIc) under the same conditions gave only 4*a*-isopropyl derivative (IIIc) in 90% yield. No conversion of IIIc by prolonged irradiation was observed. 4*a*-Isopropyl derivative (IIIc) thus formed was identical with a sample prepared in a low yield by the thermolysis of IIc in every respect.

The structures of Va, b, c were fully supported by physicochemical data, *e.g.*, the NMR spectrum of the corresponding sulfoxide of Va showed an AB-type quartet signal (DMSO-d_6, δ 3.64, 4.59, each 1H, J=12 Hz) assignable to a methylene proton adjacent to a sulfoxide grouping, while a methylene of Va showed a singlet signal (δ 3.90, 2H). The NMR spectrum of Vb ($CDCl_3$, δ 6.75 (1H, broad), 4.76 (1H, quartet, J=7.5 Hz), 1.20 (3H, doublet, J=7.5 Hz)) showed the presence of an NH group and a CH_3–CH– group.

We tentatively suggest a conceivable mechanism of the ring expansion as follows[18]: 1) The [1,2]rearrangement (photochemical orbital symmetry-allowed process) of ylides IIa, b to IIIa, b. 2) The homolytic cleavage of a C–S bond of IIIa, b, d to give a biradical intermediate (B). 3) The formation of a conjugated olefin (C) *via* the elimination of α-hydrogen atom in the 4*a*-substituents of (B) for which a thiyl radical could participate. 4) The thermal or photochemical 1,4-addition of a thiol group to the conjugated olefin in (C) leading to Va, b, c (or the photochemical 1,2-addition in *anti*-Markownikov manner followed by 1,3-hydrogen shift).

Involvement of a radical species in the reaction is relevant to depression of the ring expansion under the presence of oxygen.

No formation of the ring expansion product in the irradiation of 4*a*-isopropyl derivative (IIIc) is intriguing and puzzling. When irradiation of IIIc was carried out in methanol-d_4, no incorporation of a deuterium in the isopropyl methine group of the recovered IIIc was observed. This fact may be explained as follows: A biradical (D) could be formed initially in a similar manner to the cases of IIIa, b, d under the same conditions.[19] Contrary to the biradical (B) derived from IIIa, b, d, the biradical (D) would adopt an unfavorable conformation

14) N. Dennis, B. Ibrahim, A.R. Katritzky, and Y. Takeuchi, *Chem. Commun.*, **1973**, 292.
15) G.D. Daves, W.R. Anderson, and M.V. Pickering, *Chem. Commun.*, **1974**, 301.
16) M. Hori, T. Kataoka, and H. Shimizu, *Chemistry Letters*, **1974**, 1117.
17) J. Stackhouse, B.E. Maryanoff, G.H. Senker, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 5650 (1974).
18) The reaction mode of similar types of rearrangements involving thiols have been discussed (*cf.* J. Sheradsky "The Chemistry of the Thiol", ed. S. Patai, Wiley-Interscience, New York, Part II, 1974, p. 702). Photo-ring expansion of dihydrobenzo(*b*) thiophene to thiochroman has been observed and a possible mechanism has been presented (*cf.* D.C. Neckers and J. Dezwaan, *Chem. Commun.*, **1969**, 813).
19) 4*a*-Isopropyl derivative(IIIc) showed analogous UV spectrum to that of 4*a*-methyl derivative(IIIa) (see Experimental part).

for the hydrogen abstraction to give a conjugated olefin (E) by virtue of the bulky effect of the isopropyl group, and consequently (D) could undergo the radical-recombination to revert to IIIc. If the reversion to IIIc involves the 1,2-addition of a thiol group to a isopropylidene double bond in the intermediate (E), deuterium incorporation in the isopropyl group of IIIc should be observed.

Experimental

All melting points are uncorrected. Spectra were recorded as follows: NMR on a Hitachi R-20B 60 MHz spectrometer *vs.* internal tetramethylsilane; IR on a Hitachi 215 spectrometer; ultraviolet spectrum (UV) on a Shimadzu MPS-50L spectrophotometer; mass spectra on a JEOL JMS-0ISG spectrometer. All irradiations were conducted with a Rikosha 100W high pressure mercury arc lamp or a Rikosha 400W high pressure mercury arc lamp through a Pyrex filter. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, b=broad.

General Irradiation Procedure——A solution of the starting material in MeOH was flushed with dry nitrogen for 15 to 30 min and then irradiated for the stated time at about 15° under nitrogen with magnetic stirring.

1,3-Dimethyl-5-alkyl-2,4-dioxo-1,2,3,4-tetrahydro-5*H*-pyrimido-[5,4-*b*]-1,4-benzothiazinium Ylide (IIa, b, c)——To a stirred suspension of I (1.30 g) in dry DMF was added in portions sodium hydride (0.3 g of 50% oil dispersion) on ice cooling. After stirring for 15 min, excess methyl iodide was added to the solution and the mixture was further stirred for 30 min. The reaction mixture was poured into ice water and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over anhyd. Na_2SO_4 and evaporated under reduced pressure at room temperature. The residue was dissolved in ether (30 ml) and allowed to stand at 0° overnight. The precipitated pale green needles (IIa) (0.81 g) were collected, mp 201°. IR ν_{max}^{KBr} cm^{-1}: 1670, 1600 (CO). NMR (DMSO-d_6) δ: 2.57 (3H, s, $SC\underline{H}_3$), 3.20 (3H, s, $NC\underline{H}_3$), 3.46 (3H, s, $NC\underline{H}_3$), 7.00—7.90 (4H, m, aromatic H). *Anal.* Calcd. for $C_{13}H_{13}O_2N_3S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.74; H, 5.01; N, 15.27.

Analogously, ethyl thiazinium ylide (IIb) (0.80 g) was obtained by reaction of I (1.30 g) with ethyl iodide, as colorless needles, mp 168° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1680, 1620 (CO). NMR ($CDCl_3$) δ: 1.13 (3H, t, J=7.5 Hz, $SCH_2C\underline{H}_3$), 2.40—3.09 (2H, m, $SC\underline{H}_2CH_3$), 3.37 (3H, s, $NC\underline{H}_3$), 3.58 (3H, s, $NC\underline{H}_3$), 6.90—7.70 (4H, m, aromatic H). *Anal.* Calcd. for $C_{14}H_{15}O_2N_3S$: C, 58.12; H, 5.23; N, 14.53. Found: C, 57.93; H, 5.26; N, 14.60.

Isopropyl thiazinium ylide (IIc) (0.90 g) was also obtained by reaction of I (1.30 g) with isopropyl iodide under analogous conditions, mp 110° (decomp.), as colorless needles. IR ν_{max}^{KBr} cm^{-1}: 1680, 1630 (CO). NMR ($CDCl_3$) δ: 1.12 (3H, d, J=5 Hz, C–$C\underline{H}_3$), 1.23 (3H, d, J=5 Hz, C–$C\underline{H}_3$), 2.85—3.32 (1H, m, $C\underline{H}(CH_3)_2$), 3.37 (3H, s, $NC\underline{H}_3$), 3.58 (3H, s, $NC\underline{H}_3$), 6.95—7.70 (4H, m, aromatic H). UV λ_{max}^{EtOH} mμ (ε): 225 (28600), 258 (19300), 304 (7400), 340 (5500). *Anal.* Calcd. for $C_{15}H_{17}O_2N_3S$: C, 59.39; H, 5.65; N, 13.86. Found: C, 59.12; H, 5.54; N, 13.99.

1,3-Dimethyl-5-benzyl-2,4-dioxo-1,2,3,4-tetrahydro-5*H*-pyrimido-[5,4-*b*]-1,4-benzothiazinium Ylide (IId)——To a stirred suspension of I (1.30 g) in dry DMF was added portionwise sodium hydride (0.30 g of 50% oil dispersion) on ice cooling. After stirring for 15 min, to the resulting solution was added excess benzyl bromide and the mixture was further stirred for 10 min. The reaction mixture was poured into ice water. The deposited solid was collected, and washed with cold water and then with ethanol. Vaccum drying (below 20°) of the solid gave ylide (IId) (0.71 g) in nearly pure state, as colorless powder, mp 95° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1680, 1607 (CO). NMR ($CDCl_3$) δ: 3.38 (3H, s, $NC\underline{H}_3$), 3.45 (3H, s, $NC\underline{H}_3$), 3.73, 4.07 (2H, AB type, q, J=12 Hz, $C\underline{H}_2$), 6.70—7.70 (9H, m, aromatic H).

4*a*-Allyl-1,3-dimethyl-1,2,3,4-tetrahydro-4*a*(*H*)-pyrimido[5,4-*b*]-1,4-benzothiazine-2,4-dione (IIIe)——To a stirred suspension of I (1.30 g) in dry DMF (20 ml) was added in portions sodium hydride (0.3 g of 50% oil dispersion) with cooling in an ice bath. After stirring for 15 min, to the resulting solution was added excess allyl iodide and the mixture was kept stirring for 30 min. The reaction mixture was poured into ice water. After 3 hr, the precipitate was collected and recrystallized from ether–*n*-hexane to give IIIe (1.22 g), as colorless prisms, mp 107°. IR ν_{max}^{KBr} cm^{-1}: 1725, 1675 (CO). NMR ($CDCl_3$) δ: 2.35—2.95 (2H, m, $C\underline{H}_2$–CH=CH_2), 3.35 (3H, s, $NC\underline{H}_3$), 3.55 (3H, s, $NC\underline{H}_3$), 4.85—5.85 (3H, m, vinyl H), 7.10—7.50 (4H, m, aromatic H). *Anal.* Calcd. for $C_{15}H_{15}O_2N_3S$: C, 59.79; H, 5.02; N, 13.95. Found: C, 59.66; H, 5.07; N, 13.85.

Thermal Rearrangement of Ylide (IIa)——Ylide (IIa) (0.275 g) was heated at 210 to 220° without solvent. The resulting brown oil was chromatographed on silica gel (solvent: $CHCl_3$) to give 4*a*-methyl derivative (IIIa) (0.210 g) and N-methyl derivative (IVa) (0.010 g).

The rearranged product (IIIa) was recrystallized from *n*-hexane to give colorless prisms, mp 112°. IR ν_{max}^{KBr} cm^{-1}: 1720, 1670 (CO). NMR ($CDCl_3$) δ: 1.62 (3H, s, C–$C\underline{H}_3$), 3.38 (3H, s, $NC\underline{H}_3$), 3.58 (3H, s, $NC\underline{H}_3$), 7.00—7.50 (5H, m, aromatic H). UV λ_{max}^{EtOH} mμ (ε): 226 (26200), 261 (11700), 310 (7500). *Anal.* Calcd. for $C_{13}H_{13}O_2N_3S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.95; H, 4.80; N, 15.55. Another rearranged product (IVa)

was recrystallized from MeOH to give yellow needles, mp 192°. IR ν_{max}^{KBr} cm^{-1}: 1680, 1620 (CO). NMR ($CDCl_3$) δ: 3.32 (3H, s, NCH_3), 3.37 (3H, s, NCH_3), 3.50 (3H, s, NCH_3), 6.90—7.25 (4H, m, aromatic H). UV λ_{max}^{EtOH} mμ (ε): 222 (15600), 250 (17900), 290 (8200). *Anal.* Calcd. for $C_{13}H_{13}O_2N_3S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.58; H, 4.84; N, 15.29.

The NMR spectrum of the reaction mixture prior to chromatography showed the presences of IIIa and IVa with the ratio of about 10: 1.

Thermolysis of Ylide (IIb)——Ylide (IIb) (0.03 g) in DMSO-d_6 (0.5 ml) was heated at 150° in a sealed NMR tube and the reaction was monitored by taking NMR spectra. After 1.5 hr, methyl signals due to the starting material (IIb) disappeared. Methyl signals of the parent thiazine (I) and 4*a*-ethyl derivative (IIIb) (trace), and an olefinic proton signal of ethylene (δ 5.40) were observed, respectively. The NMR spectrum did not show the presence of other products in the reaction mixture. The major product (I) was isolated as yellow precipitate when the reaction mixture was poured into H_2O (10 ml) and identified by comparison of IR spectrum with an authentic sample.

Analogously, thermolysis of ylide (IIc) was carried out. Thiazine (I) and 4*a*-isopropyl derivative (IIIc) were isolated.

Thermal Rearrangement of Ylide (IId)——Ylide (IId) (0.35 g) in $CHCl_3$ (30 ml) was warmed at 35±5° for 2 hr. The reaction mixture was concentrated under reduced pressure and chromatographed on silica gel (solvent: $CHCl_3$) to separate IIId (0.250 g) and IVb (0.075 g).

The rearranged product (IIId) was recrystallized from EtOH to give colorless prisms, mp 144°. IR ν_{max}^{KBr} cm^{-1}: 1720, 1670 (CO). NMR ($CDCl_3$) δ: 3.04, 3.30 (2H, AB type, q, J=12 Hz, benzyl methylene protons), 3.15 (3H, s, NCH_3), 3.25 (3H, s, NCH_3), 6.70—7.60 (9H, m, aromatic H). *Anal.* Calcd. for $C_{19}H_{17}O_2N_3S$: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.78; H, 4.98; N, 11.70.

The minor product (IVb) was recrystallized from MeOH to give yellow prisms, mp 163°. IR ν_{max}^{KBr} cm^{-1}: 1690, 1640 (CO). NMR ($CDCl_3$) δ: 3.37 (3H, s, NCH_3), 3.57 (3H, s, NCH_3), 4.66 (2H, s, N-benzyl methylene protons), 6.90—7.40 (9H, m, aromatic H). UV λ_{max}^{EtOH} mμ (ε): 246 (19500), 289 (9300). *Anal.* Calcd. for $C_{19}H_{17}O_2N_3S$: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.77; H, 4.84; N, 11.86.

The thermal rearrangement of IId in $CDCl_3$ was carried out in an NMR tube at 34° in order to monitor by NMR. After 1 hr, the NMR spectrum of the reaction mixture showed the product ratio of IIId to IVb of about 3: 1, and absence of detectable amount of other products.

N-Benzyl derivative (IVb) was stable when heated for about 20 hr under the similar conditions.

Thermal Conversion of N-Benzyl Derivative (IVb) to 4*a*-Benzyl Derivative (IIId)——N-benzyl derivative (IVb) (0.03 g) in DMSO-d_6 (0.5 ml) was heated at 150° for 30 min in a sealed NMR tube. NMR spectral analysis of the reaction mixture indicated quantitative conversion of IVb to IIId under this condition.

Photorearrangement of Methyl Thiazinium Ylide (IIa)——Ylide (IIa) (0.55 g) in EtOH (200 ml) was irradiated with 100 W high pressure mercury arc lamp for 2 hr. The reaction mixture was concentrated under reduced pressure and the residue was washed with MeOH (20 ml), and recrystallized from acetone to give thiazepine (Va) (0.43 g), mp 257°, as colorless needles. IR ν_{max}^{KBr} cm^{-1}: 3400 (NH), 1700, 1630 (CO). NMR (DMSO-d_6) δ: 3.20 (3H, s, NCH_3), 3.60 (3H, s, NCH_3), 3.90 (2H, s, SCH_2–), 6.85—7.55 (4H, m, aromatic H), 8.23 (1H, b, NH). Mass Spectrum *m/e*: 275 (M^+), 242 (M^+-33). *Anal.* Calcd. for $C_{13}H_{13}O_2N_3S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.29; H, 4.80; N, 14.96.

Photorearrangement of Ethyl Thiazinium Ylide (IIb)——Ylide (IIb) (0.58 g) in EtOH (200 ml) was irradiated with 100 W high pressure mercury arc lamp for 3 hr. The irradiated solution was concentrated under reduced pressure and the residue was chromatographed on silica gel (solvent: $CHCl_3$) to separate Vb (0.40 g) and IIIb (0.08 g).

Thiazepine (Vb) was recrystallized from ether to give colorless needles, mp 150°. IR ν_{max}^{KBr} cm^{-1}: 3350 (NH), 1690, 1630 (CO). NMR ($CDCl_3$)δ: 1.20 (3H, d, J=7.5 Hz, $CHCH_3$), 3.35 (3H, s, NCH_3), 3.72 (3H, s, NCH_3), 4.76 (1H, q, J=7.5 Hz, $CHCH_3$), 6.75 (1H, b, NH), 6.93—7.66 (4H, m, aromatic H). Mass Spectrum *m/e*: 289 (M^+), 264 (M^+-25), 256 (M^+-33). *Anal.* Calcd. for $C_{14}H_{15}O_2N_3S$: C, 58.12; H, 5.23; N, 14.53. Found: C, 57.83; H, 5.25; N, 14.23.

4*a*-Ethyl derivative (IIIb) was recrystallized from *n*-hexane to give colorless prisms, mp 95°. IR ν_{max}^{KBr} cm^{-1}: 1720, 1675 (CO). NMR ($CDCl_3$) δ: 0.84 (3H, t, J=7 Hz, CH_2CH_3), 1.57—2.00 (2H, m, CH_2CH_3), 3.34 (3H, s, NCH_3), 3.54 (3H, s, NCH_3), 6.90—7.40 (4H, m, aromatic H). *Anal.* Calcd. for $C_{14}H_{15}O_2N_3S$: C, 58.12; H, 5.23; N, 14.53. Found: C, 58.37; H, 5.26; N, 14.65.

Photorearrangement of Isopropyl Thiazinium Ylide (IIc)——Ylide (IIc) (0.30 g) in MeOH (200 ml) was irradiated with 100 W high pressure mercury arc lamp for 4 hr. The irradiated solution was concentrated under reduced pressure and the residue was recrystallized from *n*-hexane to give 4*a*-isopropyl derivative (IIIc) (0.29 g) as colorless prisms, mp 111—112°. IR ν_{max}^{KBr} cm^{-1}: 1720, 1670 (CO). NMR ($CDCl_3$) δ: 0.88 (3H, d, J=7 Hz, C–CH_3), 1.03 (3H, d, J=7 Hz, C–CH_3), 1.90—2.40 (1H, m, $CH(CH_3)_2$), 3.36 (3H, s, NCH_3), 3.60 (3H, s, NCH_3), 7.00—7.45 (4H, m, aromatic H). UV λ_{max}^{EtOH} mμ (ε): 226 (25500), 261 (20100), 310 (6900). *Anal.* Calcd. for $C_{15}H_{17}O_2N_3S$: C, 59.39; H, 5.65; N, 13.86. Found: C, 59.44; H, 5.86; N, 14.14.

Photoreaction of IIc (0.015 g) in CD_3OD (0.5 ml) in a Pyrex NMR tube adjacent to the 400 W mercury arc lamp for 25 hr was monitored by taking NMR spectra. Thus, the quantitative conversion of IIc to IIIc

was proved. The NMR spectrum of the solution after further irradiation (30 hr) showed no formation of other products and no incorporation of deuterium at the isopropyl methine of IIIc.

Photolysis of 4*a*-Methyl Derivative (IIIa)——A solution of IIIa (0.28 g) in MeOH (200 ml) was irradiated for 2 hr and concentrated to dryness under reduced pressure. The residue was recrystallized from acetone to give thiazepine (0.25 g), which had an IR spectrum identical with that of an authentic sample obtained by photolysis of IIa.

Photolysis of 4*a*-Ethyl Derivative (IIIb)——A solution of IIIb (0.29 g) in MeOH (200 ml) was irradiated for 2 hr and concentrated to dryness under reduced pressure. The residue was chromatographed on silica gel (solvent: $CHCl_3$) to isolate Vb (0.20 g). Thiazepine (Vb) thus obtained was identical in every respect with an authentic sample prepared by photolysis of IIb.

Photolysis of 4*a*-Benzyl Derivative (IIId)——A solution of IIId (0.70 g) in MeOH (200 ml) was irradiated with 100 W high pressure mercury arc lamp for 4 hr. After evaporation of the solvent, the residue was washed with ether. Thus, Vc (0.52 g), colorless needles (from EtOH), mp 224°, was obtained in the pure state. IR ν_{max}^{KBr} cm^{-1}: 3350 (NH), 1690, 1620 (CO). NMR ($CDCl_3$) δ: 3.30 (3H, s, NCH_3), 3.72 (3H, s, NCH_3), 6.02 (1H, s, CH–C_6H_5), 6.60—7.10 (4H, m, aromatic H), 6.75 (1H, b, NH). *Anal.* Calcd. for $C_{19}H_{17}O_2N_3S$: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.69; H, 4.82; N, 11.89.

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